

Magnetocrystalline anisotropy and orbital polarization in ferromagnetic transition metals

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The magnetocrystalline anisotropy energies (MAEs) of the ferromagnetic metals bcc Fe, fcc and hcp Co, and fcc Ni have been calculated by using the *ab initio* tight-binding method. Disentangling the strong correlation among the *d* orbitals with the Hamiltonian in the local spin-density approximation, we have investigated the orbital polarizations induced by the Hubbard U and Racah B . The experimental MAE of fcc Ni is found with the value of U close to that determined from experiments and used in other theories. With the optimized values of U and J , both the MAEs and the orbital moments for Fe and Co are in close agreement with experiment.

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Obtaining the magnetocrystalline anisotropy energies (MAEs) of Fe, Co, and Ni from *ab initio* calculations within the local-spin-density approximation (LSDA) to density functional theory is of considerable current interest [1, 2, 3, 4, 5, 6]. From various high-quality LSDA calculations, the best case is Fe, where the computed values differ from experiment by a factor of about 2. The result for hcp Co is far worse, and for Ni, the sign is not even correct. The effect of the so called spin-other-orbit coupling is far too small to bring theory and experiment into accord [6]. The discrepancy between theory and experiment, especially in the case of Ni, is usually attributed to the LSDA.

The LSDA predicted MAEs and orbital moments can be improved for Fe and Co [2, 7] by introducing the Brooks' orbital polarization (OPB) term [8] which mimics Hund's second rule. However for Ni, the predicted easy axis is still wrong [2]. In OPB, OP is driven by the Racah parameter B , with an energy functional related to the orbital moment $\langle \hat{L} \rangle$ given by $\Delta E_{\text{OPB}} = -\frac{1}{2}B\langle \hat{L} \rangle^2$ [9]. It was argued that the key parameter responsible for the exchange-correlation enhancement of the orbital moments in solids is the Hubbard U rather than the intra-atomic Hund's second rule coupling [10]. Recently, the experimental MAEs of Fe and Ni have been obtained [5] in the LDA+ U method [11] with the noncollinearity of intra-atomic magnetization included. However, the authors found the MAE of fcc Ni to be a very rapidly varying function of U (from -50 to $60 \mu\text{eV}/\text{atom}$). A slight change of the value of U ($\sim 0.1\text{eV}$) may predict the wrong sign. Given this sensitivity, it is highly desirable to disentangle the intra-atomic strong correlation with the Hamiltonian in the LSDA and therefore to clarify the effect of OP in first principles calculations. This is the purpose of the present paper.

The basic features of the electronic structure of Fe, Co, and Ni can be understood on the basis of their two types of valence-electron orbitals [12]. The extended *s*, *p* (, and *f*) orbitals should be well described by the LSDA. The fairly localized *d* orbitals, for which the electron-electron interaction is between the localized and itinerant limits,

are not adequately dealt with in the LSDA [11]. In order to disentangle the strong correlation with the LSDA, we express the Hamiltonian as $\hat{H} = \hat{H}^{\text{LSDA}} + \hat{H}^{\text{C}} + \hat{H}^{\text{SO}}$. Here \hat{H}^{LSDA} is the standard LSDA Hamiltonian, \hat{H}^{C} is the correlation within the *d* orbital subspace and \hat{H}^{SO} the spin-orbital interaction.

We start with the LSDA Hamiltonian in the orthogonal representation of the tight-binding linear muffin-tin orbital method in the atomic sphere approximation (TB-LMTO-ASA) [13],

$$\hat{H}^{\text{LSDA}} = C + \sqrt{\Delta}S^\gamma(\mathbf{k})\sqrt{\Delta}, \quad (1)$$

where C , Δ , and γ are the self-consistent standard potential parameters. Because the electron-electron interaction is included in \hat{H}^{C} , the on-site diagonal matrix element of the *d* orbital is replaced with $C_d = (C_d^\uparrow + C_d^\downarrow)/2$. $S^\gamma(\mathbf{k})$ is the structure constant matrix in the orthogonal representation [13] with \mathbf{k} running over the Brillouin zone (BZ). \hat{H}^{LSDA} is block-diagonal in the spin index σ along the magnetization direction. The spin-orbit coupling matrix elements for *d* orbitals are calculated in the last iteration of the self-consistent field procedure [1] and \hat{H}^{SO} is treated in the usual single-site approximation [14].

Similarly to the LDA+ U method [10, 11], we treat the screened interaction among the intra-atomic *d*-orbitals in the Hatree-Fock approximation (HFA),

$$E^{\text{ee}} = \frac{1}{2} \sum_{\{m\}}^{\sigma\sigma'} n_{m_1 m_2}^\sigma (U_{m_1 m_3 m_2 m_4} - U_{m_1 m_3 m_4 m_2} \delta_{\sigma, \sigma'}) n_{m_3 m_4}^{\sigma'} - E_a, \quad (2)$$

where $U_{m_1 m_3 m_2 m_4} = \langle m_1, m_3 | V^{\text{ee}} | m_2, m_4 \rangle$ and $n_{m_1 m_2}^\sigma$ is the on-site *d* occupation matrix in the spin-orbital space. E_a is the average interaction without spin and orbital polarization. $U_{m_1 m_3 m_2 m_4}$ are determined by three Slater integrals F_0 , F_2 , and F_4 [15], which are linked to three physical parameters: the on-site Coulomb repulsion $U = F_0$, exchange $J = \frac{1}{14}(F_2 + F_4)$, and Racah parameter $B = \frac{1}{441}(9F_2 - 5F_4)$. In terms of U and J , E_a is

expressed as $\frac{1}{2}Un_d^2 - \frac{U+4J}{5}(\frac{n_d}{2})^2$, where n_d is the on-site d -orbital occupation. The ratio F_4/F_2 is, to a good accuracy, a constant ~ 0.625 for d electrons [11], which leads to the estimation $B \approx 0.11J$. The interaction energy E^{ee} , which is rotationally invariant with respect to the basis, leads to an effective potential H^C acting on the d -orbital subspace.

The spin polarization (SP) in LSDA is generically close to the Stoner concept with an energy related to spin magnetization m of $\Delta E_{SP}^{LSDA}(m) = -\frac{1}{2}I(m)m^2$, where $I(m)$ is of the order of 1 eV[16]. In the HFA, the average spin splitting for d electrons is driven by $I = \frac{1}{5}(U + 4J)$, with OP determined by $U_{eff} = U - J$ [17]. In the limit $B = 0$, $U_{m_1m_3m_2m_4}$ only involves two spherical harmonics [15], and $U = J = I$ is approximately equivalent to the LSDA [18]. Even with $U_{eff} = 0$, there is no simple relation between E^{ee} and the orbital moment $\langle \hat{L} \rangle$ [10]. In practice, the problem involving the OPs induced by the Hubbard U and Racah B can be solved numerically by working directly with the site-diagonal elements of the occupation matrix.

The MAE is calculated by taking the difference of two total energies with different directions of magnetization (MAE = $E_{111} - E_{001}$ for cubic structures and MAE = $E_{1010} - E_{0001}$ for hcp structure). The total energies are obtained via fully self-consistent solutions of \hat{H} , with the double counting corrections to the total energy included. For the \mathbf{k} -space integration, we use the special point method [19] with a Gaussian broadening of 50 meV [2]. We use 100^3 sampling points in the BZ for cubic structure and $100 \times 100 \times 56$ points for hcp structure. We have also included the occupation number broadening correction terms to the ground-state total energy [20]. Numerical convergence has been tested against the number of \mathbf{k} -points and Gaussian broadening. We first calculate the electronic structure self-consistently using the scalar relativistic TB-LMTO-ASA method. Then we construct the Hamiltonian \hat{H} , using the spin-orbital coupling constants corresponding to the d band center [1].

Considering the fact that the spin moments are well described by the LSDA, for a particular value of U , we have chosen the parameter J such that the magnetic moment maintains the theoretical value from the LSDA without spin-orbit coupling. The calculated spin moments are almost independent of B . Because the strong correlation U and J are entangled with the LSDA potential in the LDA+ U method [11], the dependence of the magnetic moment on U and J is not clear. Moreover, the energy E^{ee} defined in the LDA+ U method [10, 11] is not zero even without any SP and OP. This may render the interpretation of the delicate MAE dependence on U quite difficult. In their LDA+ U calculations of Fe and Ni, Yang et al. [5] scanned the (U, J) parameter space and obtained the path of U and J values which hold constant the theoretical magnetic moment aligned along the (001) direction. J increases with U in their parameter path, in contrast to the basic concept $\frac{U+4J}{5} \approx I_d$. The SP and OP are treated on the same footing in our HFA

scheme. The calculated MAEs versus the values of U are depicted in Fig. 1. The corresponding orbital moments are presented in Fig. 2.

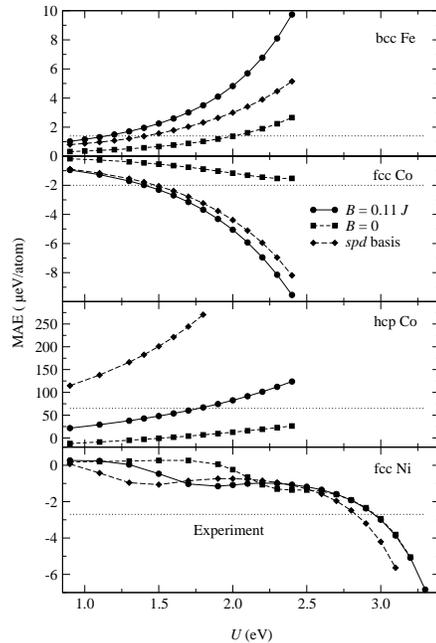


FIG. 1: MAEs of bcc Fe, fcc Co, hcp Co, and fcc Ni as a function of Hubbard U . Two curves in $spdf$ basis are plotted for each case, one with $B = 0.11J$, the other with $B = 0$. The experimental values are indicated by the horizontal dotted lines (1.4, 65, and $-2.7 \mu\text{eV}/\text{atom}$ for bcc Fe, hcp Co and fcc Ni[2], and $2.0 \mu\text{eV}/\text{atom}$ for fcc Co [21]). The MAEs calculated in $spdf$ basis with $B = 0.11J$ are also presented.

The ASA does not significantly affect the accuracy of MAE. In fact, the differences in the MAEs and orbital moments calculated by the LMTO-ASA method [1] and those calculated by the full potential (FP) LMTO method [2] are negligible if the same partial wave expansion $l_{max} = 2$ is used. In cubic structures, the difference between the MAEs with $l_{max} = 3$ and $l_{max} = 2$ is very small ($< 0.1 \mu\text{eV}/\text{atom}$)[3]. However for hcp Co, the MAE changed sign when angular momentum l_{max} increased from 2 to 3[1]. The MAE calculated in the $spdf$ LMTOs is closer to the recent accurate result calculated from FP linearized augmented plane-wave (LAPW) method [6]. Because the LMTOs in the $spdf$ basis are more complete than the ones in the spd basis[13], we regard the results in $spdf$ basis more reliable.

In the limit $B = 0$ and $U \approx J$, our calculated MAEs and orbital moments (the left ends of the $B = 0$ plots) lie in the range of the recent high quality LSDA values [1, 2, 3, 4, 5, 6]. In particular, the predicted signs of the MAEs for hcp Co and fcc Ni are wrong in the $spdf$ basis. The calculated orbital moments are about 40% smaller

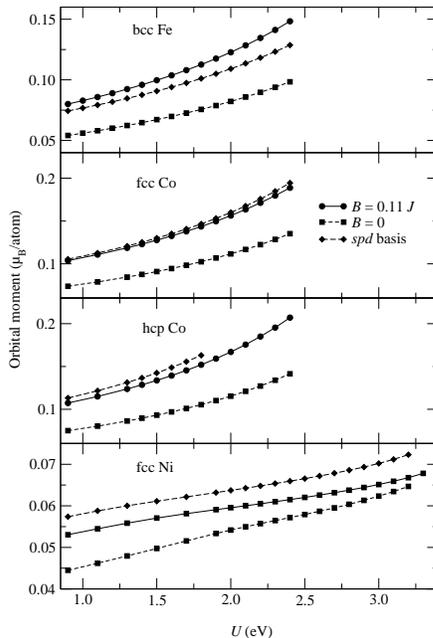


FIG. 2: Orbital magnetic moment for bcc Fe, fcc Co, hcp Co, and fcc Ni along the experimental easy axis as a function of U . The plots are labelled the same as FIG. 1.

than the experimental values for Fe and Co, while for Ni, it is very close to the experimental value. Since the LSDA is even poorer in Ni than in Fe and Co[12], the agreement must be accidental.

By turning on the orbital polarization induced by the Racah B at $U \approx J$, the calculated MAEs for Fe and Co are in much better agreement with the experimental data. This is similar to the LSDA+OPB calculations[2, 7]. Particularly, the predicted easy axis is correct for hcp Co [7]. The calculated MAE in *spdf* basis for hcp Co is quite close to that of the LMTO-ASA calculation with OPB[7], while our *spd* MAE is quite close to the FP-LMTO+OPB result[2]. Interestingly, as shown in Fig. 2, the enhancement of orbital moment due to OP induced by Racah B is in excellent agreement with the OPB calculations [2] despite the forms of E^{ee} and ΔE_{OPB} being quite different. We suggest that the widely used OPB can be brought *precisely into accord* with the unrestricted HFA with ΔE_{OPB} replaced by E^{ee} at $U = J$ ($\frac{n_d}{2}$ in E_a replaced with n_d^\uparrow and n_d^\downarrow). Only with the OP induced by B , the predicted sign of MAE for fcc Ni is wrong.

We now study the effect of OP induced by U with $U_{\text{eff}} > 0$. Similarly to the OP induced by B , as shown in Fig. 2, the OP induced by U enhances the orbital magnetic moments. For both Fe and Co, the MAEs change very smoothly and monotonically with increasing U . For Ni, the MAE is about zero when $U \approx 1.3$ eV. It de-

creases with increasing U , then making a flat region with $\text{MAE} \approx -1$ eV from $U = 1.7$ to $U = 2.5$. After the flat region, the MAE decreases with increasing U , reaching the experimental value at $U = 2.95$ eV. The MAE predicted here changes very smoothly with increasing U and with correct sign when $U > 1.3$ eV, without the strong sensitivity observed in the LDA+ U calculations [5].

TABLE I: U and J (in eV) corresponding to experimental magnetic anisotropy energy (in *spdf* basis with $B = 0.11J$). The calculated orbital moments l_z (μ_B/atom) along easy axis are compared with the experimental data [2].

	bcc Fe	fcc Co	hcp Co	fcc Ni
U	1.15	1.41	1.77	2.95
J	0.97	0.83	0.75	0.28
l_z	0.087	0.123	0.150	0.064
expt.	0.08		0.14	0.05

When $U > 2.5$ eV, the two MAE curves of $B = 0$ and $B = 0.11J$ are almost indistinguishable for fcc Ni. Thus we conclude that it is the Hubbard U that is fully responsible for bringing theory into accord with experiment. For Fe and Co, both OPs induced by U and B are needed to produce the experimental MAEs. As shown in Table I, for bcc Fe and hcp Co, the optimized U and J almost simultaneously give the experimental MAEs and orbital moments. The predicted orbital moment for fcc Ni is slightly higher, but quite acceptable. The optimized values of U and J and their trend from Fe to Ni are very similar to those determined from experiments and used in other theories [12, 22]. The optimized values of U for fcc Co and hcp Co are close but not the same. This may be due to the fact that the experimental MAE of fcc Co was extracted from measurement on supported films [21] or that the calculated MAE of hcp Co is not fully converged even with $l_{\text{max}} = 3$.

It was conjectured that the failure of the LSDA to predict the MAE of fcc Ni is related to the band structure along ΓX direction [1]. As shown in Fig.3, similarly to the LSDA bands[1], five bands cross the Fermi energy almost at the same \mathbf{k} point when $J \approx U = 0.9$ eV and $B = 0$ (The bands for $B = 0.11J$ are quite similar). One of the d bands is just above the Fermi level at the X point and results in the appearance of small X_2 pocket on the Fermi surface[1, 5], which has not been found experimentally. Increasing the valence electrons and thus pushing down the band corresponding to the X_2 pocket, Daalderop et al. [1] found the correct easy axis for fcc Ni. We find that the X_2 pocket disappears at $U \approx 1.5$ eV, corresponding to the start point of the correct sign of the MAE. With increasing U , this band is further pushed down and when $U \approx 3$ eV, it is below the Fermi energy by about 0.2 eV. In our approach, the disappearance of the X_2 pocket is a natural result of the OP induced by Hubbard U .

As a delicate property, the MAE is naturally expected

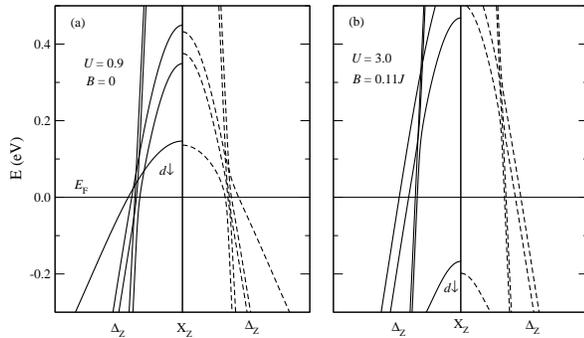


FIG. 3: Band structure of fcc Ni along $\Delta_Z = 2\pi/a(0, 0, l)$ with the spin quantization axis in the (001) (solid lines) and the (111) (dashed lines) directions. Here $0.4 \leq l \leq 1.0$. $l = 1.0$ corresponds to the X_Z point.

to depend on the delicate changes of the band structures. We have applied the current scheme to the parametrized TB models of Fe and Ni fitting to the APW bands in the LSDA [23]. The trend and optimized values of U and J are found to be very similar to the *ab initio* TB calculations. This underlines the importance of how to treat the intra-atomic strong correlation.

In summary, we have calculated the MAEs of Fe, Co, and Ni from the *ab initio* tight-binding total energies. Disentangling the strong correlation among the intra-atomic d orbitals with the Hamiltonian in the LSDA and therefore treating the SP and OP on the same footing, we have solved the long-standing notorious problem of the MAE of fcc Ni. The discussions on the OPs induced by Hubbard U and Racah B can shed light on future first principles and model TB calculations. How to calculate the interaction parameter U in metallic environment directly from first principles is still an open problem.

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