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Constituents of magnetic anisotropy and a screening of spin–orbit coupling in solids ☆

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ABSTRACT

Using quantum mechanical perturbation theory (PT) we analyze how the energy of perturbation of different orders is renormalized in solids. We test the validity of PT analysis by considering a specific case of spin–orbit coupling as a perturbation. We further compare the relativistic energy and the magnetic anisotropy from the PT approach with direct density functional calculations in FePt, CoPt, FePd, MnAl, MnGa, FeNi, and tetragonally strained FeCo. In addition using decomposition of anisotropy into contributions from individual sites and different spin components we explain the microscopic origin of high anisotropy in FePt and CoPt magnets.

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The magnetocrystalline anisotropy is a central magnetic property for both fundamental and practical reasons [1–3]. It can depend sensitively on many quantities such as dopants or small changes in lattice constant [4]. While control of this sensitive quantity can be crucial in many applications, e.g. permanent magnetism [5], magnetooptics [6] and magnetoresistive random-access memory devices [7], it is often unclear what mechanisms are responsible for these anisotropy variations, even from a fundamental point of view. It was understood long ago [8,9] that the magnetic anisotropy energy (MAE) K in bulk materials is a result of simultaneous action of spin–orbit coupling (SOC) and crystal field (CF). While in general this statement is still valid, existing microscopic methods do not accurately describe K in the majority of materials. One can calculate MAE using *ab initio* electronic structure methods based on the density functional theory, however a quantitative agreement is often rather poor. In any case such methods are usually not well equipped to resolve it into components that yield an intuitive understanding, to enable its manipulation and control. Sometimes K is analyzed in terms of SOC matrix elements of $\xi \mathbf{l} \cdot \mathbf{s}$, where ξ is the SOC constant. However, this perturbation also induces changes in other terms

contributing to the total energy, which can affect the MAE as well. Below we show how the actual atomic SOC is 'screened' in crystals and study spin decomposition of SOC and MAE in real world magnets.

Let us write the total Hamiltonian of magnetic electronic system as

$$H = H_0 + V, \tag{1}$$

where H_0 is the non-relativistic Hamiltonian (sum of kinetic and potential energies of electrons) and $V = \xi \mathbf{l} \cdot \mathbf{s}$ is the SOC Hamiltonian. We assume that ξ is small relative to CF and spin splittings. The change in the total energy of the system when SOC is added (below we call it relativistic part of the total energy) can be written as

$$E = \Delta E_0 + E_{so}, \tag{2}$$

where E_{so} is the matrix element of SOC with full perturbed wavefunction and ΔE_0 is the induced energy change of the scalar-relativistic Hamiltonian (sum of kinetic and potential energies) due to the SOC perturbation.

Using standard quantum mechanical perturbation theory (PT) each quantity $|\phi\rangle = \sum|n\rangle, E = \sum E^{(n)}$ and $E_{so} = \sum V^{(n)}$ (wave function, total energy and perturbation V) can be expressed as a sum over orders n: $V^{(n)}$ is proportional to ξ^{n+1}, while $|n\rangle$ and $E^{(n)}$ are of order ξ^n. Here and hereafter we use superscripts in parentheses to denote the order of perturbation term of the corresponding quantity. Corresponding expansions can be introduced for the total MAE and MAE due to the SOC term as $K = \sum K^{(n)}$ and $K_{so} = \sum K_{so}^{(n)}$.

If $|0\rangle$ is an eigenvector of unperturbed system (H_0) then the total perturbation energy can be found as

$$E = \sum_n E^{(n)} = \sum_n \langle 0|V|n\rangle = \langle 0|V|\phi\rangle \qquad (3)$$

(see, for instance, Eq. 5.1.37 in Ref. [10]). It is now straightforward to show that

$$E_{so} = \langle \phi|V|\phi\rangle = \sum_n n E^{(n)}, \qquad (4)$$

so the sum of kinetic and potential energies' change can be presented as

$$\Delta E_0 = \sum_n (1-n) E^{(n)} = (\langle 0| - \langle/\phi|) V|\phi\rangle. \qquad (5)$$

The last expression can be directly evaluated to estimate a reaction of the system to the original perturbation V. In our case this reaction corresponds to joint action of kinetic and potential energy terms (H_0 in Eq. (1)). Eq. (4) is particularly convenient for the analysis due to the opportunity to obtain site and spin decompositions.

Let us consider again a specific case of SOC perturbation $V = \xi \mathbf{l} \cdot \mathbf{s}$ in the second order of PT. In this case we have $E^{(2)} = E_{so}^{(1)}/2 = V^{(1)}/2$, where $V^{(1)}$ is obtained using wave function of the first order $|\phi\rangle \approx (|0\rangle + |1\rangle)$. Correspondingly, for the second order MAE

$$K^{(2)} = K_{so}^{(1)}/2. \qquad (6)$$

The second order correction to the total MAE due to SOC is a half of the first order MAE due to SOC only. It is a simple consequence of our perturbation treatment. One can immediately write down the MAE in cubic systems where the leading term scales as ξ^4, as $K^{(4)} = K_{so}^{(3)}/4$. Thus kinetic and potential terms effectively 'screen' 75% of the original SOC MAE in cubic materials. Evidently higher order contributions to total MAE decrease as $1/n$ relative to SOC anisotropy. Thus the highest anisotropy can be naturally expected only for a small n.

The specific form of the second order correction due to SOC has been studied many times in different parts of solid state physics [1,8,9,11] and can be obtained if we rewrite $V^{(1)}$ as

$$V^{(1)} = 2\langle 0 \left| \xi \mathbf{l} \cdot \mathbf{s} \right| 1\rangle = 2\xi s_i^{(0)} l_i^{(1)} = 2\xi s_i^{(0)} \sum_{exc} \frac{\langle 0|l_i|1\rangle\langle 1|\xi s_j l_j|0\rangle}{\varepsilon' - \varepsilon_0}$$
$$= 2\xi^2 s_i^{(0)} \sum_{exc} \frac{\langle 0|l_i|1\rangle\langle 1|l_j|0\rangle}{\varepsilon' - \varepsilon_0} s_j^{(0)} = 2\xi s_i^{(0)} \Lambda_{ij} s_j^{(0)}, \qquad (7)$$

where we indicated the specific orders for spin and orbital moments entering $V^{(1)}$, ε_0 and ε' are the ground state and the excited state energy respectively for the unperturbed system, and the sum is over all excited states. The leading relativistic correction for the spin moment s appears only in the second order in ξ and does not contribute to $V^{(1)}$. Below we assume that s does not change from its zero order value. This result (Eq. (7)) is the familiar expression [1,8,9,11] for the second order spin Hamiltonian due to SOC, where orbital moment tensor $\Lambda = l^{(1)}/\xi s$. Correspondingly, in the uniaxial system (assuming $\Lambda_{\nu\mu}$ is diagonal) we have $K^{(2)} = \xi s(l_z^{(1)} - l_x^{(1)}) = \xi^2 s^2 (\Lambda_\perp - \Lambda_\parallel)$.

One can regard the total relativistic energy as the energy change due to the 'atomic' SOC (i.e. matrix elements of $\xi \mathbf{l} \cdot \mathbf{s}$), 'screened' or reduced by adjustments in other contributions to the total energy. The same evidently holds true for the total relativistic energy change relative to SOC energy alone even in the nonmagnetic case. One can rewrite Eq. (2) as

$$E = \Delta E_0 + \langle \xi \mathbf{l} \cdot \mathbf{s}\rangle = \langle \tilde{\xi} \mathbf{l} \cdot \mathbf{s}\rangle \qquad (8)$$

where $\tilde{\xi}$ is a screened or effective crystal SOC constant as opposed to the atomic or nonrenormalized ξ. We call $\tilde{\xi}/\xi$ ratio *spin–orbit reduction* factor. One can compare this parameter with the enhancement of SOC discussed in Ref. [12].

According to the above results (Eq. (4)) $\tilde{\xi} = \xi/2$ (second order correction) and $\tilde{\xi} = \xi/4$ (fourth order correction). Thus the effective screening is minimal for systems with large SOC and non-cubic symmetries. Evidently this conclusion supports traditionally large anisotropies observed in magnetic uniaxial systems.

Thus H_0 term in Eq. (1), the sum of kinetic and potential energies, reduces the effect of SOC and makes overall strength twice smaller in second order, so $K_{kin} + K_{pot} = -K_{so}/2$. Overall the action of these terms is destructive for materials with observed uniaxial anisotropy as total K is opposite in sign to the anisotropy induced by kinetic and potential terms together: $K = -(K_{kin} + K_{pot})$. Also comparing Eqs. (4) and (5) one can see that for arbitrary n ratio $E_{so}^{(n)}/E_0^{(n)} = n/(1-n)$, thus for large n this ratio tends to be equal to -1 meaning that SOC effects are nearly completely screened in this limit.

Let us now consider electronic structure calculations for realistic systems. Using the Vienna ab initio simulation package [13] method we obtained the relativistic energy $E = (E_r - E_{nr})$ and SOC energy E_{so} in non-magnetic and magnetic systems, where E_{nr} and E_r are total energies obtained in scalar relativistic and calculations where SOC has been added (relativistic). The SOC is included [14] using the second-variation procedure. The generalized gradient approximation of Perdew, Burke, and Ernzerhof was used for the correlation and exchange potentials. The nuclei and the core electrons were described by projector augmented wave potentials and the wave functions of valence electrons were expanded in a plane-wave basis set with a energy cutoff between 348 eV and 368 eV for all compounds we investigated in this work. The k-point integration was performed using a tetrahedron method with Blöchl corrections with 13 800 k-points in the first Brillouin zone corresponding to the primitive unit cell of L1$_0$ structure.

We compared the spin–orbit reduction factor $\alpha = E_{so}/E$ for Al and non-magnetic Fe. The resulting α appears to be very close to 2 with small deviations of about 1–3%. For magnetic systems, we also found that $\alpha \approx 2$ for different magnetization directions.

MAE in L1$_0$ compounds and tetragonal FeCo had been well studied [2,3,15–18]. The calculated MAE values are in a reasonable agreement with previous calculations [2,3]. For CoPt, the discrepancy between current calculation and previous ones is rather large. This is due to the exchange correlation potential used, our LDA calculation gives a MAE about 1.3 meV/f.u., which is in better agreement with previous calculations.

Here we investigated K_{so}/K in those systems and the results are presented in Table 1. The anisotropic part of E_{so} appears to be much smaller than the isotropic part, and deviations of K_{so}/K from 2 are already significant. For instance K_{so}/K in CoPt is 1.67–1.8 depending on the exchange-correlation potential used. Compared with E_{so}, K_{so} is a much smaller quantity. The deviations of K_{so}/K from the factor two in Table 1 are related to a deviation from a second order PT. That includes both self-consistency effects and a contribution from higher order terms of PT.

Table 1

c/a ratio (with respect to the primitive cell), calculated K and K_{so}/K ratio in uniaxial magnetic systems. For all systems experimental structures have been used, while for FeCo, we used hypothetical tetragonally strained structure.

Compounds	c/a	K (μeV/f.u.)	K_{so}/K
FePt	1.362	2661	1.84
CoPt	1.379	837	1.67
FeNi	1.414	87	1.98
FePd	1.370	174	2.14
MnAl	1.294	287	1.98
MnGa	1.280	437	1.99
FeCo	1.1	216	2.21