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Possible definition of atom- and bond-resolved contributions to the magnetocrystalline anisotropy energy

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Two notes on the interpretation of the magnetocrystalline anisotropy energy are given. First, methods to define atom-resolved contributions to the magnetocrystalline anisotropy energy of compounds are scrutinized. Second, a method concerning bond-resolved contributions is introduced which is able to test Kittel's famous interpretation of the magnetocrystalline anisotropy energy.

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I. INTRODUCTION

The magnetocrystalline anisotropy energy is a key quantity for the technological application of magnetic materials. A more fundamental understanding of this material parameter would be very helpful to find guidelines for the design of devices with special properties, especially for nanostructured and multicomponent systems. In the present Brief Report we want to give a contribution in this direction. In Sec. II we will comment on the attempts to define atom-resolved contributions to the magnetocrystalline anisotropy energy. There are numerous situations for which such a decomposition of the magnetocrystalline anisotropy energy of the whole system into contributions of individual atoms would be helpful. For instance, it has been found in recent years that the magnetic properties of ferromagnetic metal films[1] or nanoparticles[2] may be modified by applying an electric field or by electrolytically charging the system. By means of atom-resolved contributions it is possible to separate the modifications of the surface and bulk anisotropy and, thus, to supplement already existing more phenomenological fitting procedures.[3] In addition, it is possible to separate the effects on various types of atoms in multicomponent systems. The magnetic anisotropy is a relativistic effect resulting from the spin-orbit coupling, and in detail it is influenced by hybridization effects (see Sec. III), chemical order, structural relaxation, etc.[4] Therefore, the atom-resolved contributions are meaningful just for the specific system under consideration. It is of course not possible to define a contribution of a given atom which could be used as an intrinsic property of that atom in different surroundings. In Sec. III, we define bond-resolved contributions to the magnetocrystalline anisotropy energy which can be used to test Kittel's famous interpretation of that energy.

II. ATOM-RESOLVED CONTRIBUTIONS TO THE MAGNETOCRYSTALLINE ANISOTROPY ENERGY

Because of the relativistic effect of spin-orbit coupling the electronic energy E^d of a magnet with collinear magnetization is different for different directions of the magnetization (superscript d) in the crystal, it is lowest for the magnetization in the easy (E^e) directions and largest for the magnetization in the hard (E^h) directions. We define the magnetocrystalline anisotropy energy E_{mca} as $E_{\mathrm{mca}}=E^h-E^e$. For many systems, especially for those with reduced symmetry, E^h and E^e, and hence E_{mca} can be calculated highly accurately within the framework of the *ab initio* spin-density-functional electron theory, either in a fully relativistic version or on the level of Pauli-Kohn-Sham equations in which the spin-orbit coupling term is incorporated. We do not want to assess critically the accuracy of such calculations, but we want to comment on the physical interpretation of the results which may be obtained by them.

The central quantity of the spin-density functional theory is the spin-density matrix $\underline{\underline{\rho}}(\mathbf{r})$ from which the electron density $n(\mathbf{r})$ can be obtained via $n(\mathbf{r})=\mathrm{Tr}\underline{\underline{\rho}}(\mathbf{r})$. The spin-density matrix is calculated from the single-electron spinor fields $\boldsymbol{\Psi}_n(\mathbf{r})$ with the components $\Psi_{n,i}(\mathbf{r})$, $i=1,2$,

$$\rho_{ij}(\mathbf{r})=\sum_n f_n\Psi_{n,i}(\mathbf{r})\Psi^*_{n,j}(\mathbf{r}), \tag{1}$$

with the Fermi-Dirac occupation numbers f_n. The $\boldsymbol{\Psi}_n(\mathbf{r})$ are determined from the Pauli-Kohn-Sham equations

$$\left(-\frac{\hbar^2}{2m}\Delta\underline{\underline{I}}+\underline{\underline{H}}^{\mathrm{SO}}+\underline{\underline{W}}_{\mathrm{eff}}\right)\boldsymbol{\Psi}_n=\varepsilon_n\boldsymbol{\Psi}_n, \tag{2}$$

where $\underline{\underline{I}}$ is the unity matrix, ε_n denotes the single-electron energies, $\underline{\underline{H}}^{\mathrm{SO}}$ is the spin-orbit coupling operator, and $\underline{\underline{W}}_{\mathrm{eff}}$ represents the effective potential matrix

$$\underline{\underline{W}}_{\mathrm{eff}}=(V_{\text{e-n}}+V_{\mathrm{H}})\underline{\underline{I}}+\underline{\underline{W}}_{\mathrm{xc}}. \tag{3}$$

In the Eq. (3) $V_{\text{e-n}}$ is the Coulomb interaction energy between the electrons and the nuclei with charge $Z_\alpha e$ at position $\mathbf{R}_\alpha$

$$V_{\text{e-n}}=\sum_\alpha\frac{Z_\alpha e^2}{|\mathbf{r}-\mathbf{R}_\alpha|}, \tag{4}$$

V_{H} is the Hartree potential

$$V_{\mathrm{H}}=\frac{\delta E_{\mathrm{H}}}{\delta n(\mathbf{r})}=e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r', \tag{5}$$

and $\underline{\underline{W}}_{\mathrm{xc}}$ is the exchange-correlation matrix

$$\underline{\underline{W}}_{\mathrm{xc}}=\frac{\delta E_{\mathrm{xc}}}{\delta\underline{\underline{\rho}}(\mathbf{r})}, \tag{6}$$

with the Hartree energy E_{H} and the exchange-correlation energy E_{xc}. In the present Brief Report we do not consider spin-dependent external potentials.

Starting point for our considerations are the two equivalent expressions for the electronic energy of the spin-density functional electron theory. The first one is

$$E = T + E_{\mathrm{H}} + E_{\mathrm{xc}} + E_{\text{e-n}}. \tag{7}$$

Here T is the kinetic energy,

$$T = \sum_n f_n \int \mathbf{\Psi}_n^*(\mathbf{r})\left(-\frac{\hbar^2}{2m}\Delta\right)\mathbf{\Psi}_n(\mathbf{r})d^3r, \tag{8}$$

and $E_{\text{e-n}}$ is given by

$$E_{\text{e-n}} = \int n(\mathbf{r})V_{\text{e-n}}(\mathbf{r})d^3r. \tag{9}$$

The second form is

$$E = \sum_n f_n \varepsilon_n + E_{\mathrm{H}} + E_{\mathrm{xc}} + E_{\text{e-n}} - \int \underline{\underline{\rho}}(\mathbf{r})\underline{\underline{W}}_{\mathrm{eff}} d^3r. \tag{10}$$

One question of interest is whether it is possible to subdivide in a physically meaningful manner the total magnetocrystalline anisotropy energy into local contributions from various regions of real space, e.g., into atom-resolved contributions for the case of multicomponent compounds. At least formally this can be achieved[1] when using Eq. (7) for the total energy, because all terms are real-space integrals which can be subdivided into integrals over individual volume elements. (Please note, however, that there is some ambiguity in this procedure because the results depend on the choice of the sizes and forms of these individual volume elements.) Problems arise when starting from the total energy expression (10) because here the first term, the band-structure energy $\Sigma_n f_n \varepsilon_n$, is not given by an integral in real space. In the literature it has been attempted to represent the magnetocrystalline anisotropy energy using the magnetic force theorem by the difference between the band-structure energies for the two magnetization directions h and e and by introducing the atom-resolved densities of states for a subdivision of the band-structure energy into atom-resolved contributions. We want to show that this is not possible without a serious ambiguity.

The quantities E^h and E^e are in principle determined by two self-consistent spin-density functional calculations for the two magnetization directions h and e. Usually, however, the computational effort can be reduced by using the magnetic force theorem[5,6] which provides good results by estimating the differences of total energies subtracting the band energies. When using the magnetic force theorem, a self-consistent calculation is performed just for one direction, say e, yielding the single-electron energies and the occupation numbers f_n^e and the self-consistent spin-density matrix $\underline{\underline{\rho}}^e$. Then the rigidly rotated $\underline{\underline{\rho}}^e$ (rotation matrix R) is used as the input spin-density matrix $\underline{\underline{\rho}}_{\mathrm{in}}^h = R^{-1}\underline{\underline{\rho}}^e R$ for the one-shot calculation with magnetization in the direction h. It is assumed that $\underline{\underline{\rho}}_{\mathrm{in}}^h$ is a good approximation for the spin-density $\underline{\underline{\rho}}^h$ which would be calculated self-consistently for the magnetization direction h. With the input effective potential matrix $\underline{\underline{W}}_{\mathrm{eff}}[\underline{\underline{\rho}}_{\mathrm{in}}^h]$ the Kohn-Sham equations are solved just once, yielding the non-self-consistent (nsc) energies $\varepsilon_n^{h,\mathrm{nsc}}$, the corresponding occupation numbers $f_n^{h,\mathrm{nsc}}$ and a non-self-consistent density matrix $\underline{\underline{\rho}}^{h,\mathrm{nsc}}$ which differs from $\underline{\underline{\rho}}^h$ by $\delta\underline{\underline{\rho}} = \underline{\underline{\rho}}^h - \underline{\underline{\rho}}^{h,\mathrm{nsc}}$. The magnetic force theorem then tells that E_{mca} can be approximated by

$$\begin{aligned} E_{\mathrm{mca}} &= \sum_n f_n^{h,\mathrm{nsc}}\varepsilon_n^{h,\mathrm{nsc}} - \sum_n f_n^e \varepsilon_n^e + \mathcal{O}(\delta\underline{\underline{\rho}}^2) \\ &= \int_{-\infty}^{\varepsilon_F^{h,\mathrm{nsc}}} z^{h,\mathrm{nsc}}(\epsilon)\epsilon d\epsilon - \int_{-\infty}^{\varepsilon_F^e} z^e(\epsilon)\epsilon d\epsilon + \mathcal{O}(\delta\underline{\underline{\rho}}^2), \end{aligned} \tag{11}$$

where ε_F^e and $\varepsilon_F^{h,\mathrm{nsc}}$ denote the Fermi energies and $z^e(\epsilon)$ and $z^{h,\mathrm{nsc}}(\epsilon)$ are the densities of states for the orientation e and h, respectively.

The basic idea is that the densities of states $z^d(\epsilon)$ (d=e or h, nsc) can be subdivided into atom-resolved quantities,

$$z^d(\epsilon) = \sum_i z_i^d(\epsilon), \tag{12}$$

where the index i labels the various atoms, for instance, the Fe and Pt atom in the $L1_0$ compound FePt. Inserting Eq. (12) into Eq. (11) yields (omitting the superscript nsc)

$$E_{\mathrm{mca}} = \sum_i E_{\mathrm{mca},i}, \tag{13}$$

with

$$E_{\mathrm{mca},i} = \int_{-\infty}^{\varepsilon_F^h} z_i^h(\epsilon)\epsilon d\epsilon - \int_{-\infty}^{\varepsilon_F^e} z_i^e(\epsilon)\epsilon d\epsilon. \tag{14}$$

When performing a partial integration of Eq. (14) and assuming that the densities of states are approximately constant in the range $|\varepsilon_F^h - \varepsilon_F^e|$ around $\varepsilon_F = \frac{\varepsilon_F^h + \varepsilon_F^e}{2}$ we obtain

$$E_{\mathrm{mca},i} = F_i^e(\varepsilon_F) - F_i^h(\varepsilon_F) + \varepsilon_F \Delta N_i, \tag{15}$$

with

$$F_i^d(\varepsilon_F) = \int_{-\infty}^{\varepsilon_F} d\epsilon' \int_{-\infty}^{\epsilon'} d\epsilon'' z_i^d(\epsilon''), \tag{16}$$

and

$$\Delta N_i = \int_{-\infty}^{\varepsilon_F^h} d\epsilon z_i^h(\epsilon) - \int_{-\infty}^{\varepsilon_F^e} d\epsilon z_i^e(\epsilon). \tag{17}$$

The quantity ΔN_i denotes the change of the number of electrons at the atom i induced by the change of the magnetization direction from the easy to the hard direction.

The quantities $F_i^d(\varepsilon_F)$ have the important property that they are invariant against a rigid shift of all energies. First, the integral

$$\tilde{z}_i^d(\epsilon') = \int_{-\infty}^{\epsilon'} d\epsilon'' z_i^d(\epsilon''),$$

is invariant because the lower edges of $z_i^d(\epsilon'')$ and the energy ϵ' shift in the same manner. Second, the integral

$$F_i^d(\varepsilon_F) = \int_{-\infty}^{\varepsilon_F} d\epsilon' \tilde{z}_i^d(\epsilon'), \tag{18}$$

is also invariant, because ε_F exhibits the same shift as the lower band edges. This is due to the fact that $\varepsilon_F = \frac{\varepsilon_F^h + \varepsilon_F^e}{2}$ and that ε_F^d are determined via

$$N_{\mathrm{el}} = \int_{-\infty}^{\varepsilon_F^d} d\epsilon z_i^d(\epsilon), \tag{19}$$

with the total number N_{el} of occupied electronic states which is the same for the two directions h and e of the magnetization. Unfortunately, however, the last term in Eq. (15) is not invariant because the invariant quantity ΔN_i is multiplied by the noninvariant quantity ε_F. In the literature it has been suggested[7] to consider the $E_{\mathrm{mca},i}$ as atom-resolved contributions to the magnetic anisotropy energy, but in fact these quantities suffer from the ambiguity introduced by the dependence of $\varepsilon_F \Delta N_i$ on the arbitrary choice of the energy zero. (Note that because of charge conservation the total magnetocrystalline anisotropy energy calculated by applying the magnetic force theorem is independent of the choice of energy zero.) On the other hand it has been suggested[8,9] to consider the quantities $F_i^e(\varepsilon_F) - F_i^h(\varepsilon_F)$ as atom-resolved contributions. As discussed above, these differences indeed do not depend on the choice of energy zero. However, they do not have a simple physical meaning because they neglect the unavoidable electron transfer ΔN_i. Altogether, it therefore must be concluded that it is not possible to define physically meaningful atomic contributions to the magnetic anisotropy energy when starting from the total energy expression (10). As an example, we have calculated by means of the LMTO-ASA bandstructure method,[10] the charge transfer between the Fe atom and the Pt atom in the $L1_0$ compound FePt when changing the direction of the magnetization from the easy to the hard direction. The charge in the two atomic spheres thereby changes by $\Delta N_{Fe} = -\Delta N_{Pt} = 0.0004$ electrons. This, however, does not say anything about the relative importance of the term $\varepsilon_F \Delta N_i$ in the Eq. (15) because due to the complete arbitrariness in the choice of energy zero the averaged Fermi energy ε_F can take any value.

III. BOND-RESOLVED CONTRIBUTIONS-ON KITTEL'S INTERPRETATION OF THE MANGNETOCRYSTALLINE ANISOTROPY ENERGY

In his book, "Introduction to Solid State Physics" Kittel[11] has given an interpretation of the physical origin of the magnetocrystalline anisotropy energy which is illustrated in Fig. 1. The upper part of this figure shows a sketch of a system with the magnetization oriented in the easy direction. In this situation those electronic orbitals are occupied which exhibit an optimum overlap and hence lead to an optimum covalent bond energy. The lower part of the figure shows the situation with the magnetization in the hard direction, thereby assuming for simplicity that the spin-orbit coupling is extremely large. Then the spin-orbit coupling enforces the occupation of electronic orbitals which do not exhibit an optimum overlap and hence belong to a lower covalent bond energy. Obviously, in Kittel's model the magnetocrystalline anisotropy energy is related to the fact that in a system with spin-orbit coupling the covalent bond energy depends on the orientation of the magnetization in the crystal. In the following we outline a method which is able to determine this anisotropy of the covalent bond energy and which therefore provides a tool to test Kittel's interpretation of the magnetocrystalline anisotropy energy.

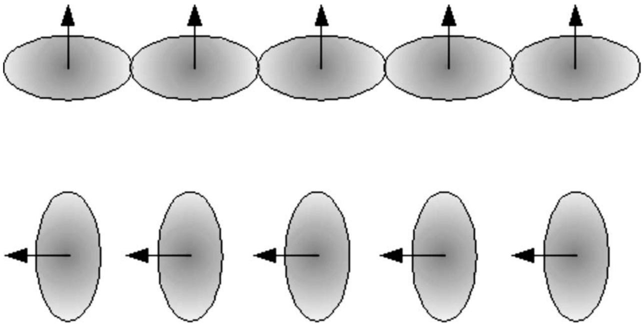

FIG. 1. A schematic visualization of Kittel's interpretation of the magnetocrystalline anisotropy energy (see text).

In the following, we consider the cohesive energy E_{c}, defined by

$$E_{\mathrm{c}} = E + E_{\mathrm{cc}} - E^{\mathrm{free\ atoms}}, \tag{20}$$

where E is the electronic energy [Eqs. (7) and (10)], E_{cc} represents the interaction energy between the nuclei and $E^{\mathrm{free\ atoms}}$ denotes the total energy of atoms before being condensed to the crystal. Furthermore, we expand the Bloch functions $\boldsymbol{\Psi}_n$ in a set of well-localized nonorthogonal orbitals $\phi_{i\alpha}$,

$$\boldsymbol{\Psi}_n = \sum_{i\alpha} c_n^{i\alpha} \phi_{i\alpha}, \tag{21}$$

where α describes the angular and magnetic atom quantum numbers l and m and the index i labels the various atoms. As shown in Refs. 12 and 13 (and in references therein), the cohesive energy E_{c} then may be represented by six terms, all of them having a well-defined physical meaning. Among these terms is the covalent bond energy

$$E_{\mathrm{cov}} = \sum_{\substack{i\alpha j\beta \\ i \neq j}} E_{\mathrm{cov},i\alpha j\beta}, \tag{22}$$

with

$$E_{\mathrm{cov},i\alpha j\beta} = \sum_n f_n c_n^{i\alpha} (c_n^{j\beta})^* [H_{j\beta i\alpha} - S_{j\beta i\alpha} \bar{\varepsilon}_{j\beta i\alpha}], \tag{23}$$

$$\bar{\varepsilon}_{j\beta i\alpha} = \tfrac{1}{2}(H_{i\alpha i\alpha} + H_{j\beta j\beta}), \tag{24}$$

and the overlap and Hamiltonian matrices $S_{j\beta i\alpha}$ and $H_{j\beta i\alpha}$. The covalent bond energy of an atom i is then given by the sum over all bond strengths to all surrounding atoms j

$$E_{\mathrm{cov},i} = \sum_{\alpha,j\beta} E_{\mathrm{cov},i\alpha j\beta}. \qquad (25)$$

$E_{\mathrm{cov},i\alpha j\beta}$ can be further subdivided into energy-resolved contributions,

$$E_{\mathrm{cov},i\alpha j\beta}(E) = \sum_{n} \delta(E-\varepsilon_n) f_n c_n^{i\alpha}(c_n^{j\beta})^{*}[H_{j\beta i\alpha} - S_{j\beta i\alpha}\bar{\varepsilon}_{j\beta,i\alpha}]. \qquad (26)$$

All these quantities, E_{cov}, $E_{\mathrm{cov},i\alpha j\beta}$, $E_{\mathrm{cov},i\alpha j\beta}(E)$, and $E_{\mathrm{cov},i}$ have the attractive property that they do not depend on the choice of the energy zero. Among the six contributions to the cohesive energy, E_{cov} is the only one which involves matrix elements between orbitals on different atoms, and therefore it clearly represents the contribution of the interatomic bonding. According to Kittel's model the dependence of E_{cov} on the orientation of the magnetization in the crystal should represent the major reason for the magnetocrystalline anisotropy energy, whereas the dependence of the other five terms should be of minor importance. To test Kittel's model one could, e.g., consider the $L1_0$ compound FePt and calculate both the magnetocrystalline anisotropy energy $E_{\mathrm{mca}}=E^h-E^e$ (by use of Eqs. (7) and (10)) and the anisotropy of the covalent bond energy $\Delta E_{\mathrm{cov}}=E^h_{\mathrm{cov}}-E^e_{\mathrm{cov}}$ for various values of the c/a ratio, to see whether ΔE_{cov} represents a major contribution to E_{mca} and whether the trend in $E_{\mathrm{mca}}(\mathrm{c/a})$ as determined in Ref. 14 is similar to the trend in $\Delta E_{\mathrm{cov}}(\mathrm{c/a})$.

To calculate E_{cov}, a set of fixed atom-localized orbitals has to be used which do not depend on the orientation of the magnetization. In the framework of the tight-binding linear-muffin-tin-orbital method (TB-LMTO),[10] e.g., this is not the case because there the basis orbitals are optimized for each configuration of the system, i.e., the orbitals are different for different orientations of magnetization. Because the minimal basis set of the TB-LMTO represents a noncomplete and nonorthogonal basis set, the use of two different sets of basis functions may spoil the results for ΔE_{cov}, and this may become numerically relevant in view of the fact that the values of E_{mca} and ΔE_{cov} are very small. We also want to warn against the use of the magnetic force theorem for the calculation of ΔE_{cov} where one would perform a self-consistent calculation of E_{cov} for, say, the easy direction and then make a one-shot calculation of E_{cov} for the hard direction which would involve the basis functions optimized for the easy direction. Then the demand to use the same basis set for the two magnetization directions is fulfilled. But the magnetic force theorem is designed to yield an optimum estimate for the total energy, whereas in general it does not lead to optimized expansion coefficients $c_{i\alpha}$ which, however, are required in Eqs. (23) and (26). Instead of starting from the very beginning with a band-structure method based on atom-localized orbitals one could also use a method with delocalized basis functions (such as the plane waves of a pseudopotential calculation) and project the so-obtained Bloch functions on a set of fixed atom-localized functions.[12,13] Altogether, we hope that our Brief Report will stimulate other groups working with appropriate band-structure techniques (we personally do not have codes with the above-described properties) to test Kittel's interpretation of the magnetocrystalline anisotropy energy with the tool ΔE_{cov} suggested in this Brief Report.

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