

Electron theory of magnetoelectric effects in metallic ferromagnetic nanostructures

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The physics of magnetoelectric effects in metallic films is investigated by use of the *ab initio* spin density functional theory for Fe films and Fe-Au-Fe heterofilms with various thicknesses. Based on the magnetic force theorem for the calculation of the magnetocrystalline anisotropy energy, E_{mca} , a method for the definition of layer-resolved contributions to E_{mca} is introduced, and the reliability of this method is discussed in detail. The knowledge of such layer-resolved contributions is important for a theoretical modeling of magnetoelectric effects on an atomic level in systems that are too complicated for an *ab initio* treatment. Quantities that characterize the anisotropic electron charge density and its magnetoelectric modification are introduced, and these quantities are useful for the interpretation of the magnetoelectric effects on E_{mca} in the spirit of Kittel's explanation of E_{mca} . Finally, it is shown that for certain average thicknesses of ultrathin Fe films in Fe-Au-Fe it is possible to switch the magnetization between in-plane and out-of-plane directions by rather small electric fields.

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I. INTRODUCTION AND OUTLINE

Nanostructured materials like real nanoparticles or films with nanometer thickness may exhibit exciting magnetic properties. Among these are the magnetoelectric effects, i.e., the influence of external electric fields on magnetic quantities like the size of magnetic moments or the magnetocrystalline anisotropy energy. The interest in these effects is twofold. First, it is a great scientific challenge to understand the physics of the interaction between electric and magnetic degrees of freedom. Second, it is a great technological challenge for the field of spintronics to control the magnetic properties not only by magnetic fields or spin-polarized currents but by electric fields, e.g., a switching of the magnetization by electric fields with ultralow-energy power consumption in information-processing and -storage technologies.

The materials in which the magnetoelectric effects have been investigated may be subdivided into two classes. In the first class the primary effect of the electric field probably is a spin-dependent electronic polarization. Examples are metallic magnetic films¹ of Fe-Pt and Fe-Pd or nanoparticles² of Co-Pd alloys, both with interfaces to an electrolyte or with heterostructures³⁻⁵ composed of insulators (like MgO) and magnetic (e.g., Fe) and nonmagnetic (e.g., Au) metals as used for magnetic tunnel junctions. It is assumed that the large magnetoelectric effect in the latter systems results from an enhancement of the electronic polarization of Fe at the Fe-MgO interface due to the contact with the dielectrical surface polarization of the MgO interface layer (an additional effect of an electric-field-induced displacement of Fe atoms in a possibly formed interfacial FeO layer is discussed in Ref. 6). It should be noted that for the experimentally observed magnetoelectric change of the magnetic moments of nanoparticles in an electrolyte another possible mechanism has been suggested in Ref. 2, namely an electrostrictive-magnetostrictive mechanism. In the second class⁷⁻¹⁰ there is a coupling between ferroelectric and magnetic properties, e.g., in multiferroics or in heterostructures formed by ferroelectric and magnetic materials. In these systems the primary effect of the electric field is a displacement of atoms that then modifies the magnetic properties.

Concerning theory for the first class of materials, a density-functional treatment of the magnetoelectric effects on the magnetic moments and on the magnetocrystalline anisotropy energy in thin metallic films has been performed in Ref. 11. This reference may be considered as predecessor of our present paper, in which we make further contributions to the interpretation of the spin-dependent electronic polarization effect on the magnetoelectric properties by density functional calculations for Fe films and for Fe-Au-Fe films. Thereby, we explore the magnetoelectric effect on the magnetocrystalline anisotropy by use of two methods. First, we introduce a method to subdivide the total magnetoelectric effect on the system into layer-resolved contributions. Such a layer- (or site-) resolved interpretation of the magnetoelectric effect is very important for the theoretical investigation of such systems (e.g., faceted nanoparticles) that are too complex for a full *ab initio* treatment. For such systems the effect may be investigated by a parametrization of the magnetic energy on the atomic level with a model that contains Heisenberg interatomic exchange interactions, dipolar interactions, the magnetocrystalline anisotropy energy for the bulk atoms and for the atoms near the surface (or interface), and so on. The parameters of such a model, e.g., those describing the magnetocrystalline anisotropy energies for various atoms near the surface, may be modified by an electric field. Our layer-resolved interpretation of the magnetoelectric effect will provide a method to determine these electric-field dependent parameters with the help of *ab initio* calculations, for instance, for the modeling of faceted nanoparticles. Second, we relate the magnetoelectric effect on the magnetocrystalline anisotropy energy to electric-field-induced changes of the symmetry of the electron density. A final objective of our paper is the following. It is known (see, e.g., Ref. 11) that the magnetoelectric effects in ferromagnetic metal films are significant only for large electric fields, i.e., very large electric fields are usually required to switch the magnetization from the in-plane alignment (favored by dipolar shape anisotropy) to the out-of-plane alignment (favored by the electric-field-dependent surface magnetocrystalline anisotropy). We show that for very thin layers of Fe on an Au substrate the total magnetic anisotropy (composed of the

shape anisotropy and the magnetocrystalline anisotropy) is small and may be switched in sign by relatively small fields.

II. THEORY

A. Description of our density-functional methods

We performed *ab initio* density functional calculations using the full-potential linearized augmented plane wave method¹² as implemented in the FLEUR code.¹³ In this code the system is represented by a supercell which is repeated periodically in lateral directions but not in the direction normal to the film. Experimentally, a magnetoelectric effect is generated by electric fields that are produced either by electrolytically charging the sample² or directly by a capacitor with a magnetic film on one plate.³ In the FLEUR code, primarily the effects produced by charging the sample are investigated. However, we will show in the following that the magnetoelectric effect of an external electric field also can be calculated by use of this code. The basic idea is that in the experiment an external electric field induces charges at the surface of a metallic body (which lead to an additional electric field compensating the external field in the interior of the metal). When a single metallic film is in an external electric field perpendicular to the film surfaces, the electric field then induces the movement of electrons from one surface (which then has a positive net charge formed by electrons and nuclei) to the other surface (which then has a negative net charge), and at each surface a magnetoelectric effect is generated by the electronic surface charges. Instead, in the FLEUR code we consider a metallic film for which the total number of electrons per surface atom is modified by ΔN_{el} . For $\Delta N_{\text{el}} < 0$ ($\Delta N_{\text{el}} > 0$) this means a removal (an addition) of electrons to the film, leading to a change of the net charge per surface atom (formed by electrons and nuclei) of the film by $\Delta q > 0$ ($\Delta q < 0$). In the experiment the situation with additional charge of just one sign is realized, e.g., when the magnetic film is on one plate of a capacitor. The additional charges are then localized at the free surface of the film, whereas the surface contacting the capacitor does not exhibit additional charges. If the film is thick enough, then the two surfaces do not influence each other, and we thus can study, with the FLEUR code, the magnetoelectric effect generated by the electronic surface charges induced by the electric field. In order to avoid a diverging electrostatic Ewald energy for the supercells repeated periodically in lateral directions, each supercell as a whole must have zero net charge. In Ref. 14 this is achieved by changing the nuclear charges at the surface layers in such a way that this compensates in net the change of the electronic surface charges. In the FLEUR code the neutrality of the supercell is achieved by the introduction of two layers that exhibit a δ -shaped charge density with the charge $-\Delta q$ per surface atom, respectively; see Fig. 1.

For each density functional calculation Δq is fixed, but the electron density of the charged metal film is calculated self-consistently (and the density of the additional charge appears close to the surface of that film). In contrast, the charge density of the two additional layers is fixed in the calculations, and this density is localized in such a distance to the metallic film that the electron density leaking out of the film into the vacuum is

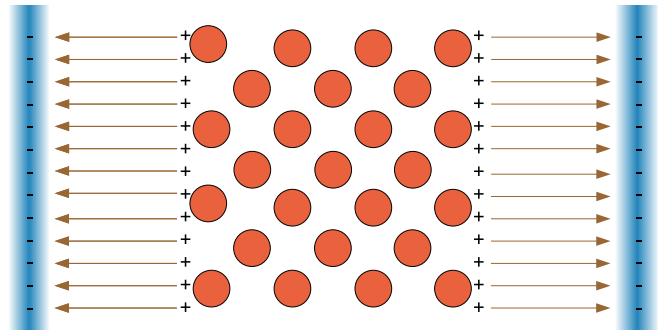


FIG. 1. (Color online) Illustration of the super cell of the charged metal film. The electric field (arrows) arises between the surface charge (+) on the metal film, which consists of muffin-tin spheres and interstitial region in between, and the neutralizing charge sheets (-).

close to zero at the position of these two layers. As indicated in Fig. 1 the surface charge density of the film and the additional δ -shaped charge densities generate electric fields in the vacuum in between. Its strength is given by $E = \epsilon_0 \frac{\Delta q}{\text{area of a surface atom}}$, where ϵ_0 is the dielectric vacuum constant. For instance, for the (001) Fe films we have $E = 0.660 \text{ V/\AA}$ for $\Delta q = 0.03$. This means that in all our following figures we could give on the abscissa the electric-field strengths instead of the charges Δq of the film. However, we will discuss everything as function of Δq , because we are mainly interested in the magnetoelectric effects of the charges Δq produced by electrolytically charging the sample or induced by an external electric field.

The in-plane components of the atom positions of the film are fixed to the values they have in the respective layers of bcc Fe and fcc Au. The out-of-plane components of the atom positions were relaxed by the use of atomic forces for zero external electric field, and they were fixed when charging the films. In general the relaxation will differ slightly for the charged films, but it is generally assumed (see, e.g., Ref. 14) that this has only a minor influence on the magnetoelectric effect. Indeed, we found by test calculations that the effect of the additional charge Δq on the out-of-plane components of atomic positions is very small and has only a tiny influence on the magnetocrystalline anisotropy energy (thereby, according to the prescription of Ref. 15, we had to subtract the relaxation effect due to the electroelastic interaction between the charge per surface atom Δq of the film and the charges $-\Delta q$ of the two neutrality-generating layers that do not appear in a real experiment). The calculations were performed with the generalized gradient approximation.¹⁶

For our films with (001) orientation we calculate the magnetocrystalline anisotropy energy E_{mca} as the difference between the total electronic energies $E_{\text{total}}(\langle 001 \rangle)$ and $E_{\text{total}}(\langle 100 \rangle)$ found for the orientations of the magnetization in the out-of-plane $\langle 001 \rangle$ direction and the in-plane $\langle 100 \rangle$ direction, $E_{\text{mca}} = E_{\text{total}}(\langle 100 \rangle) - E_{\text{total}}(\langle 001 \rangle)$. To save computer time, we use the magnetic force theorem for the calculation.¹⁷ To do this, we perform a self-consistent calculation for the ferromagnetic system in scalar-relativistic (SR) approximation, i.e., by neglecting the spin-orbit coupling (SOC). Then we determine the Kohn-Sham eigenvalues $\epsilon_{j\mathbf{k}}(\langle 001 \rangle)$ and $\epsilon_{j\mathbf{k}}(\langle 100 \rangle)$, where j is the band index and \mathbf{k} is the electron wave vector, for systems

with SOC and magnetization in the (001) and (100) directions by a respective one-shot solution of the Kohn-Sham equations with the self-consistent SR potential. The quantity E_{mca} is then given by the difference of the so-obtained band energies

$$E_{\text{mca}} = \sum_{j\mathbf{k}} \varepsilon_{j\mathbf{k}}(\langle 001 \rangle) \omega_{j\mathbf{k}}(\langle 001 \rangle) - \sum_{j\mathbf{k}} \varepsilon_{j\mathbf{k}}(\langle 100 \rangle) \omega_{j\mathbf{k}}(\langle 100 \rangle), \quad (1)$$

where $\omega_{j\mathbf{k}}$ are the Fermi-Dirac occupation numbers.

We have tested that our results have a good convergence with respect to the convergence parameters of the method. The Brillouin zone integrations have been performed with the Fermi-smearing method. Thereby, the irreducible Brillouin zone of the system with SOC is larger than the one of the system without SOC. To achieve a rapid convergence of E_{mca} with respect to the number $N_{\mathbf{k}}$ of \mathbf{k} points used for sampling of the irreducible Brillouin zone it is important to choose the respective \mathbf{k} points in such a way that the set of \mathbf{k} points used for the sampling of the larger Brillouin zone contains all the \mathbf{k} points that have been used for the sampling of the smaller zone. Consequently, for the Fe film a good convergence was found for about 7000 \mathbf{k} points in the full Brillouin zone. A good convergence with respect to the cutoff wave vector \mathbf{K}_{max} for the plane waves of the FLAPW method was obtained for $K_{\text{max}} = 3.6 \text{ a.u.}^{-1}$.

B. Definition of layer-resolved contributions

We first discuss a possible definition of layer-resolved contributions to the total magnetoelectric effect. To do this we first give possible definitions of layer-resolved contributions to the total magnetocrystalline anisotropy energy. In Ref. 18 it has been outlined that this can be done when starting from the representation of the density-functional electronic energy as a space integral over the electronic energy density; Eqs. (7)–(9) of Ref. 18. It should be noted that this real-space decomposition is not completely unambiguous as it depends on the shape of the integration cells around the various atoms. This is the method proposed in Ref. 19; however, no detailed discussion of the layer-resolved contributions is given there. More often, the total electronic energy is represented by the sum of the band energy (given by the sum of the occupied single-electron energies $\varepsilon_{j\mathbf{k}}$) and a double-counting term. When using, in addition, the magnetic force theorem, the magnetocrystalline anisotropy energy is then given by our Eq. (1). In the literature attempts have been made to introduce atom-resolved contributions to E_{mca} by representing the sums in Eq. (1) by the integrals involving the densities of states and by subdividing the densities of states into atom-resolved quantities. However, it has been shown¹⁸ that this introduces a great ambiguity for the so-defined atom-resolved magnetocrystalline anisotropies, and this ambiguity is related to the fact that the choice of the energy zero for the single-electron energies is completely arbitrary. We use a method for the introduction of atom-resolved magnetocrystalline anisotropy energies suggested in Ref. 20. This method does not suffer from that arbitrariness, but we will show that it is also not exact. Nevertheless, it produces meaningful results at least for the pure Fe films we have investigated. It should be noted that in Ref. 11 layer-resolved contributions to E_{mca} are defined via

a simplified Bruno's relation between the magnetocrystalline anisotropy energy and the orbital-moment anisotropy, but no detailed discussion of the contributions of various layers are given.

Following the suggestion of Ref. 20 we introduce layer-resolved contributions to E_{mca} by switching on the SOC operator \hat{H}^{SOC} for the calculation of the single-electron energies and occupation numbers in Eq. (1) not for all atoms of the system but, respectively, just for the atoms of one atomic layer. We denote the various layers by the superscript ν , where $\nu = 1$ is for the outermost layer of the film and increasing numbers ν are for the layers with increasing distance from the outermost layer. This procedure is possible because the SOC operator is a local operator, and in the FLEUR code the SOC is taken into account only within the muffin-tin spheres but not in the interstitial regions. We denote the single-electron energies and the occupation numbers for the SR situation in which there is no SOC for all layers by $\varepsilon_{j\mathbf{k}}^{\text{SR}}$ and $\omega_{j\mathbf{k}}^{\text{SR}}$, the corresponding quantities for the SOC switched on just for the layer ν by $\varepsilon_{j\mathbf{k}}^{\nu}$ and $\omega_{j\mathbf{k}}^{\nu}$, and the quantities for systems with SOC at all layers by $\varepsilon_{j\mathbf{k}}$ and $\omega_{j\mathbf{k}}$, and we define

$$\varepsilon_{j\mathbf{k}}^{\nu} = \varepsilon_{j\mathbf{k}}^{\text{SR}} + \Delta\varepsilon_{j\mathbf{k}}^{\nu}; \quad \varepsilon_{j\mathbf{k}} = \varepsilon_{j\mathbf{k}}^{\text{SR}} + \Delta\varepsilon_{j\mathbf{k}}, \quad (2)$$

$$\omega_{j\mathbf{k}}^{\nu} = \omega_{j\mathbf{k}}^{\text{SR}} + \Delta\omega_{j\mathbf{k}}^{\nu}; \quad \omega_{j\mathbf{k}} = \omega_{j\mathbf{k}}^{\text{SR}} + \Delta\omega_{j\mathbf{k}}. \quad (3)$$

The SR eigenvalues $\varepsilon_{j\mathbf{k}}^{\text{SR}}$ are determined by the self-consistent solution of the SR Kohn-Sham equations

$$\hat{H}^{\text{SR}} \psi_{j\mathbf{k}}^{\text{SR}} = \varepsilon_{j\mathbf{k}}^{\text{SR}} \psi_{j\mathbf{k}}^{\text{SR}}. \quad (4)$$

The eigenvalues $\varepsilon_{j\mathbf{k}}^{\nu}$ and $\varepsilon_{j\mathbf{k}}$ are determined by the one-shot solutions (see above) of the Kohn-Sham equations

$$(\hat{H}^{\text{SR}} + \hat{H}^{\text{SOC},\nu}) \psi_{j\mathbf{k}}^{\nu} = \varepsilon_{j\mathbf{k}}^{\nu} \psi_{j\mathbf{k}}^{\nu} \quad (5)$$

and

$$\left(\hat{H}^{\text{SR}} + \sum_{\nu} \hat{H}^{\text{SOC},\nu} \right) \psi_{j\mathbf{k}} = \varepsilon_{j\mathbf{k}} \psi_{j\mathbf{k}}. \quad (6)$$

It is clear that the deviations $\Delta\varepsilon_{j\mathbf{k}}^{\nu}$ do not simply add up to the deviations $\Delta\varepsilon_{j\mathbf{k}}$, i.e., the equation

$$\Delta\varepsilon_{j\mathbf{k}} = \sum_{\nu} \Delta\varepsilon_{j\mathbf{k}}^{\nu} \quad (7)$$

does not hold strictly, because the presence or absence of the SOC in one layer also influences the shape of the wave function in the other layers; see also Ref. 20. This holds especially when the atoms for which the SOC is switched on and off are heavy atoms that thus have a large SOC (see Sec. III B). Equation (7) would be strictly valid if we could confine ourselves to a calculation of $\Delta\varepsilon_{j\mathbf{k}}$ in the first order of a perturbation theory,

$$\Delta\varepsilon_{j\mathbf{k}} = \langle \psi_{j\mathbf{k}}^{\text{SR}} | \sum_{\nu} \hat{H}^{\text{SOC},\nu} | \psi_{j\mathbf{k}}^{\text{SR}} \rangle, \quad (8)$$

but it can be shown that these expectation values vanish for systems with collinear atomic magnetic moments that we consider (see, e.g., Ref. 21).

Because of the same reason, the deviations $\Delta\omega_{jk}^v$ also do not simply add up to the deviations $\Delta\omega_{jk}$, i.e., the equation

$$\Delta\omega_{jk} = \sum_v \Delta\omega_{jk}^v \quad (9)$$

also does not hold strictly. Nevertheless, inserting Eqs. (2), (3), (7), and (9) into Eq. (1), and neglecting terms of the type $\Delta\varepsilon_{jk}^v \Delta\omega_{jk}^v$, we find

$$E_{\text{mca}} = \sum_v E_{\text{mca}}^v, \quad (10)$$

with the layer-resolved contributions

$$E_{\text{mca}}^v = \sum_{jk} \varepsilon_{jk}^v \langle\langle 001 \rangle\rangle \omega_{jk}^v \langle\langle 001 \rangle\rangle - \sum_{jk} \varepsilon_{jk}^v \langle\langle 100 \rangle\rangle \omega_{jk}^v \langle\langle 100 \rangle\rangle. \quad (11)$$

This derivation clearly shows that the subdivision of the magnetocrystalline anisotropy energy into layer-resolved contributions is not strictly valid. We will show, however, that Eq. (10) holds with satisfactory accuracy in Fe films. Furthermore, we will show that E_{mca} and E_{mca}^v depend on the additional charge in a nearly linear manner, and we thus introduce the “anisotropy voltages”

$$U_{\text{mca}} = \left. \frac{\partial E_{\text{mca}}}{\partial q} \right|_{q=0} \quad (12)$$

$$U_{\text{mca}}^v = \left. \frac{\partial E_{\text{mca}}^v}{\partial q} \right|_{q=0}. \quad (13)$$

C. Characterization of the anisotropic electron charge density

We now discuss the physical mechanisms that are responsible for the magnetoelectric effect on E_{mca} induced by the spin-dependent electronic polarization in metallic films. The basis is to start from models for E_{mca} and to investigate how the electric field changes the quantities appearing in these models. The investigation in Ref. 11 starts from Bruno’s²² relation between E_{mca} and the anisotropy of the magnetic orbital moments that holds if several preconditions are fulfilled. Unfortunately, it is not discussed in Ref. 11 whether this is really the case for the investigated metallic films. Our discussion is based in Kittel’s interpretation²³ of the physical origin of E_{mca} (see Fig. 1 of Ref. 18). In this interpretation the covalent bond energy between neighboring atoms depends on the orientation of the magnetization in the crystal, because in a system with SOC the occupation of electronic orbitals changes with the orientation of the magnetization. For an orientation in the easy direction those electronic orbitals that exhibit an optimum overlap are occupied and hence lead to an optimum covalent bond energy, whereas for an orientation in the hard direction the SOC enforces the occupation of electronic orbitals that do not exhibit an optimum overlap and hence belong to a lower covalent bond energy. In Refs. 3 and 24 it has been suggested that the electric field leads to a modification of the relative occupation of the various electronic orbitals (and hence to a modification of the covalent bond energy), especially of the various $3d$ orbitals in Fe, Co, or Ni, and that this results in a magnetoelectric effect on E_{mca} .

In Refs. 25 and 26 the electric-field-induced modifications of the electronic band structure that are related to a modification of the occupation numbers of various electronic orbitals are investigated. In Ref. 18 Kittel’s explanation of E_{mca} via the covalent bond energy has been cast in a strict mathematical form called E_{cov} method.²⁷ In principle, this tool can be used to define layer- or atom-resolved contributions to E_{mca} and to investigate quantitatively the magnetoelectric effect on E_{mca} . However, the use of E_{cov} requires some effort to implement special tools into the band-structure code. Instead, we now want to characterize the anisotropic electron charge density that is related to the covalent bond energy (and which changes with the orientation of the magnetization and hence is related to E_{mca}) by simple quantities defined via the occupation numbers of various electronic orbitals. We will investigate whether these quantities evaluated for each atomic layer v are related to the E_{mca}^v , and we will show that their changes by the application of electric fields are indeed related to the magnetoelectric effect on E_{mca}^v .

In the FLAPW method the single-electron crystal wave functions are represented within the muffin-tin spheres in a basis of orbitals that are proportional to spherical harmonics. Thus the occupation numbers N_{el} for these orbitals can be determined. In a system with cubic symmetry the t_{2g} orbitals d_{xy} , d_{xz} , and d_{yz} are degenerate, $N_{\text{el}}(d_{xy}) = N_{\text{el}}(d_{xz}) = N_{\text{el}}(d_{yz})$; the e_g orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ are degenerate, $N_{\text{el}}(d_{x^2-y^2}) = N_{\text{el}}(d_{3z^2-r^2})$; and the p orbitals are also degenerate, $N_{\text{el}}(p_x) = N_{\text{el}}(p_y) = N_{\text{el}}(p_z)$. The degeneracy is broken when going from the bulk to a film with free surfaces, and when an external electric field is switched on. If the surface normal and the external electric field are along the z direction, then $N_{\text{el}}(d_{xy}) \neq N_{\text{el}}(d_{xz}) = N_{\text{el}}(d_{yz})$, $N_{\text{el}}(d_{x^2-y^2}) \neq N_{\text{el}}(d_{3z^2-r^2})$, and $N_{\text{el}}(p_z) \neq N_{\text{el}}(p_x) = N_{\text{el}}(p_y)$. As measures for this symmetry reduction we introduce the quantities

$$\Delta^{t_{2g}} = |N_{\text{el}}(d_{xy}) - N_{\text{el}}(d_{xz})|, \quad (14)$$

$$\Delta^{e_g} = |N_{\text{el}}(d_{x^2-y^2}) - N_{\text{el}}(d_{3z^2-r^2})|, \quad (15)$$

$$\Delta^p = |N_{\text{el}}(p_x) - N_{\text{el}}(p_y)|. \quad (16)$$

Of course, these quantities can be evaluated also separately for each atomic layer v , yielding $\Delta^{t_{2g},v}$, $\Delta^{e_g,v}$, and $\Delta^{p,v}$. Finally, we introduce the charge derivatives of these quantities,

$$C^i = \left. \frac{\partial \Delta^i}{\partial q} \right|_{q=0}, \quad (17)$$

with $i = t_{2g}, e_g, p, (t_{2g},v), (e_g,v), (p,v)$. We thereby calculate the $\Delta^{i,v}$ and $C^{i,v}$ in the scalar-relativistic approximation, because the scalar-relativistic charge densities enter the magnetic force theorem for the calculation of the E_{mca} (see Sec. II A).

It should be noted that it is very difficult or even impossible to derive a general quantitative relation between Kittel’s explanation of E_{mca} via the covalent bond energy and the anisotropies Δ^i of the orbital occupations for the following reason. It is clear that, in Kittel’s view, a magnetocrystalline anisotropy appears only if the charge densities around the atoms are not spherically symmetric. Therefore, our Δ^i

(which is calculated in the scalar-relativistic approximation) are measures for the precondition for a noncubic anisotropy. However, E_{mca} is related to the change of the covalent bond energy when changing in the systems with SOC the orientation of the magnetization, and therefore there is no quantitative link between E_{mca} and the Δ^i (although it is, of course, expected that the uniaxial E_{mca} is large for large Δ^i). It will be shown in Sec. III C via numerical results that the quantities E_{mca}^v nevertheless show a similar behavior as the function of v in the quantities $\Delta^{i,v}$ and the same holds for the quantities U_{mca}^v and $C^{i,v}$. This may be considered as support for the intuitive suggestion of Refs. 3 and 24 (see above).

An electric-field-induced modification of the occupation numbers for the various orbitals is discussed also in Refs. 19, 25, and 26. However, no quantities characterizing the anisotropic electron charge density (like our Δ^i) and their magnetoelectric modifications (like our C^i) are introduced, and we think that such quantities are helpful for the explanation of the magnetoelectric effect on E_{mca} in the spirit of Kittel's interpretation of the magnetocrystalline anisotropy energy.

III. RESULTS

A. Magnetoelectric effect on E_{mca} in Fe films

In Fig. 2 we show the magnetocrystalline anisotropy energy per surface atom as a function of the additional charge²⁸ Δq for nonrelaxed [Fig. 2(a)] and relaxed [Fig. 2(b)] Fe films with (001) orientation for different numbers N_L of atom layers. Therefore, only the results for positive Δq (corresponding to $\Delta N_{\text{el}} < 0$) are given, and for $\Delta q < 0$ we found results that can be represented very well by inflecting the data for $\Delta q > 0$ at the origin. For bulk Fe the E_{mca} as defined in Eq. (1) is zero because $\varepsilon_{jk}^v(\langle 001 \rangle) = \varepsilon_{jk}^v(\langle 100 \rangle)$ and $\omega_{jk}^v(\langle 001 \rangle) = \omega_{jk}^v(\langle 100 \rangle)$. For the film E_{mca} is nonzero. Without relaxation $E_{\text{mca}}/(\text{surface atom})$ should converge to a finite value with increasing N_L because for very thick films the two surfaces of the film do not interact with each other, and additional layers in the interior of the film do not contribute to E_{mca} because they see bulklike surroundings. Figure 2 shows that this convergence is rather slow and that $E_{\text{mca}}(N_L)/(\text{surface atom})$ exhibits a nonmonotonic behavior. In Ref. 29 such a behavior is related to Friedel-like oscillations of the electronic charge density resulting from quantum-well states. For a relaxed very thick film (with infinite lateral extension) there is a constant tetragonal distortion in the interior. Therefore, each additional layer in the interior of the film contributes to E_{mca} , and $E_{\text{mca}}/(\text{surface atom})$ does not converge to a constant value with increasing N_L . We nevertheless show also the results for the relaxed films [Fig. 2(b)] because of the interesting fact that for the relaxed films the oscillations of E_{mca} are smaller than for nonrelaxed films, and this certainly has to do with the fact that the influence of the quantum-well states is reduced because the distances between the relaxed atom layers are not uniform.

Because E_{mca} varies linearly with increasing Δq (especially for the nonrelaxed films), we can characterize the magnetoelectric effect on E_{mca} by the above-defined anisotropy voltage U_{mca} . Figure 3 also shows that U_{mca} exhibits a nonmonotonic dependence on N_L , which is stronger for the relaxed film. When in an experiment the film is produced by molecular

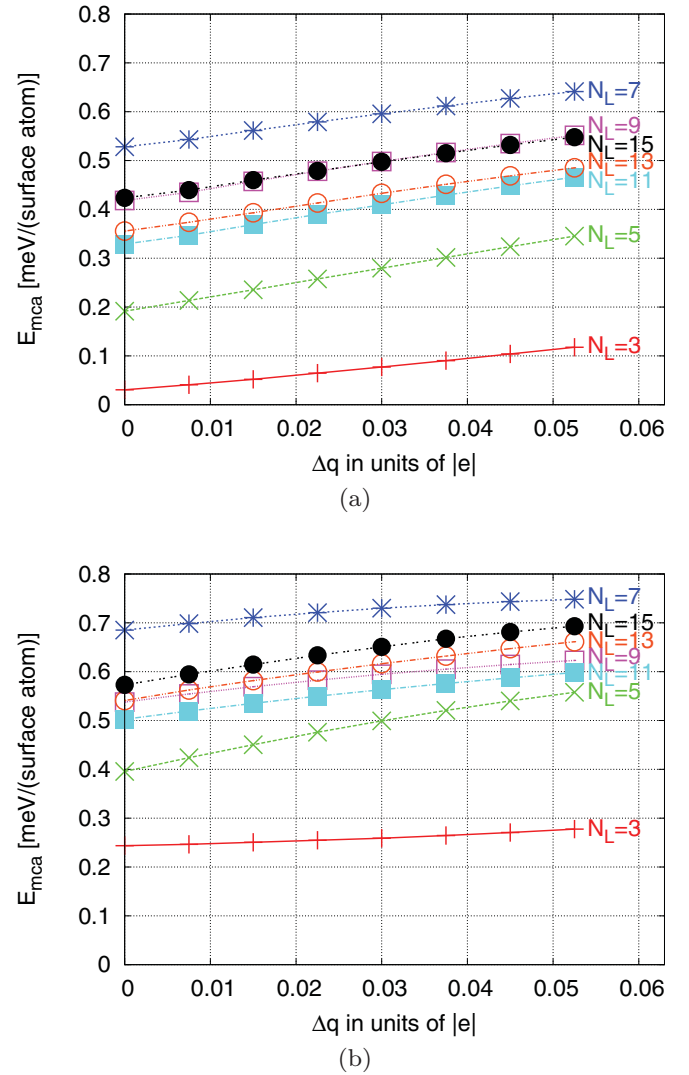


FIG. 2. (Color online) E_{mca} per surface atom for nonrelaxed (a) and relaxed (b) Fe (001) films as a function of additional charge Δq for different numbers of atomic layers N_L (e represents the elementary charge).

beam epitaxy the average film thickness does not necessarily correspond to integer numbers of atom layers.³ Therefore, we want to characterize the “typical” strength of the magnetoelectric effect by an average \bar{U}_{mca} of the values of U_{mca} given in Fig. 3, yielding $\bar{U}_{\text{mca}} = 2.42$ mV for the nonrelaxed films and $\bar{U}_{\text{mca}} = 2.23$ mV for the relaxed films. In the experiment of Ref. 3 it was found that for a Fe (001) film grown on an Au film and covered by a MgO film the quantity $E_{\text{mca}}/(\text{surface atom})$ changes by $4 \mu\text{eV}$ when applying an electric field of 200 V that changes the number of electrons per Fe surface atom at the Fe-MgO interface by 0.002. From our $\bar{U}_{\text{mca}} = 2.23$ mV we find for $\Delta q = 0.002$ a change of $E_{\text{mca}}/(\text{surface atom})$ by $4.46 \mu\text{eV}$, in good agreement with the experimental value.

B. Layer-resolved contributions

Figure 4 shows the layer-resolved magnetocrystalline anisotropies E_{mca}^v [Fig. 4(a)] and the layer-resolved anisotropy voltages U_{mca}^v [Fig. 4(b)] for nonrelaxed Fe films with different

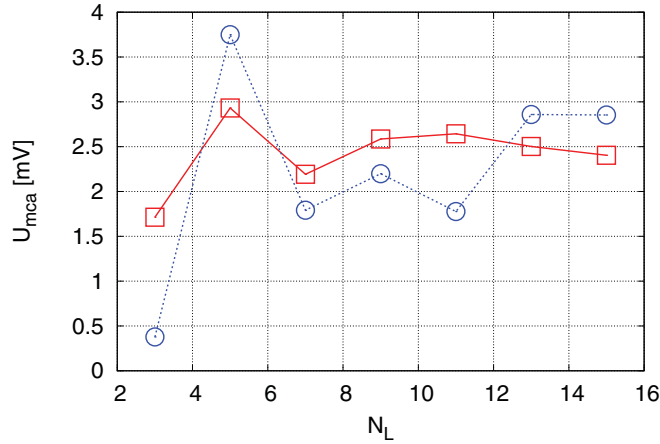


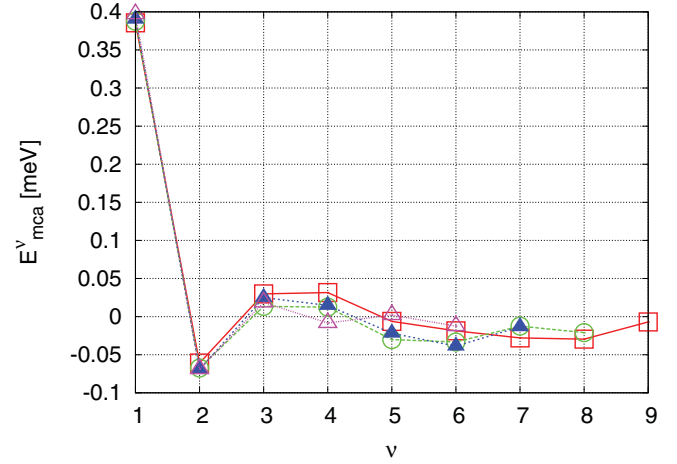
FIG. 3. (Color online) The anisotropy voltages³⁰ in mV for nonrelaxed (\square) and relaxed (\circ) Fe films as functions of the number of atom layers N_L .

numbers N_L of atom layers. The E_{mca}^ν are by far largest for the surface layer, but they are non-negligible also for layers with greater distance from the surface, and they show a nonmonotonic behavior as a function of ν . In contrast, the U_{mca}^ν are more strongly localized at the surface layer. The sum $\sum_\nu E_{mca}^\nu$ deviates from the quantity E_{mca} that we get when switching on the SOC simultaneously for the atoms of all layers, and the deviations are 6, 23, 21, and 25%; for $N_L = 11, 13, 15$, and 17. The deviations of $\sum_\nu U_{mca}^\nu$ from the quantity U_{mca} are 22, 20, and 23%; for $N_L = 9, 11$, and 13. This demonstrates that the layer-resolved contributions do not simply add up, as discussed above. However, for Fe films the deviations are not very large, and thus the subdivision into layer-resolved contributions defined by Eq. (11) does make sense and is helpful for a modeling of the systems on an atomic level.

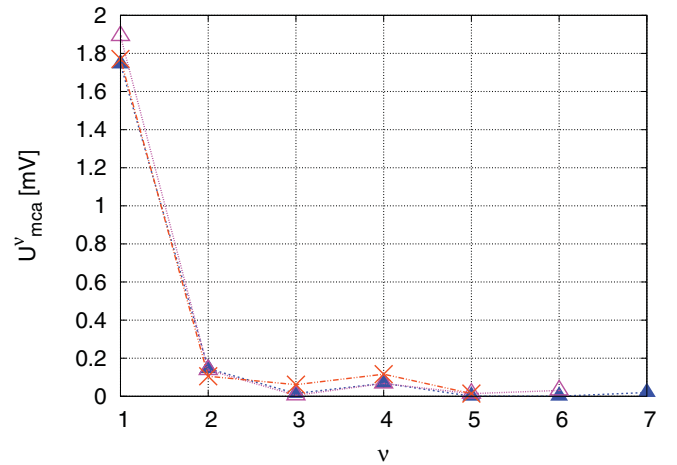
For the Fe-Au-Fe films (see Sec. III D) the subdivision into layer-resolved additive contributions does not work well, and this results from the large SOC for the heavy Au atoms (see Sec. II B). For instance, for the system with seven Au layers covered on both surfaces with two Fe layers, the sum $\sum_\nu U_{mca}^\nu$ deviates from the U_{mca} by 95%. Furthermore, switching on the SOC only for the outermost Au atoms produces a large magnetocrystalline anisotropy energy (comparable with the values obtained by switching on the SOC for the Fe atoms), although these Au atoms carry only a very small induced magnetic moment. This shows that this large magnetocrystalline anisotropy energy does not indicate a strong direct anisotropy contribution of the Au atoms themselves, but it results from the large modification of the shape of the wave functions at the Fe atoms when switching on the SOC only at the Au atoms.

C. Anisotropy of the orbital-occupation numbers

Figure 5 shows the quantities $\Delta^{i,\nu}$ [Fig. 5(a)] and $C^{i,\nu}$ [Fig. 5(b)] for the nonrelaxed Fe film. For a relaxed film these quantities would not converge to zero for increasing ν , because of the constant tetragonal distortion in the interior of the film (see Sec. III A). The data of Fig. 5(a) are for $\Delta q = 0.03$ electrons/(surface atom), for other values of Δq the curves



(a)



(b)

FIG. 4. (Color online) Layer-resolved E_{mca}^ν (a) and U_{mca}^ν (b) in Fe $\langle 001 \rangle$ films with $N_L = 9$ (\times), $N_L = 11$ (\triangle), $N_L = 13$ (\blacktriangle), $N_L = 15$ (\circ), and $N_L = 17$ (\square) (only the values for nonequivalent atoms are shown).

look qualitatively similar. At least close to the surface the values of $\Delta^{t_{2g},\nu}$ are larger than those of $\Delta^{e_g,\nu}$ and $\Delta^{p,\nu}$ (which, however, are also considerable for small ν). They are largest for the surface layer, but they are non-negligible also for layers with greater distance from the surface, and they show a nonmonotonic behavior as a function of ν . All this resembles the behavior of the E_{mca}^ν shown in Fig. 4(a). In contrast, the $C^{t_{2g},\nu}$ are more strongly localized at the surface layer, and their behavior as function of ν resembles very much the one of U_{mca}^ν . The $C^{e_g,\nu}$ and $C^{p,\nu}$ are very small. Obviously the effect of an electric field is by far strongest for the anisotropy of the occupations of the d - t_{2g} orbitals, i.e., the magnetoelectric effect on the magnetocrystalline anisotropy energy may be related to the magnetoelectric effect on the anisotropy in occupation of these orbitals.

Figure 2(a) (and Fig. 7) shows that for the nonrelaxed Fe films the quantity E_{mca} per surface atom is maximum for $N_L = 7$. We have calculated $\Delta^{t_{2g},1}$ for various N_L , and indeed we found a maximum for $N_L = 7$. This demonstrates,

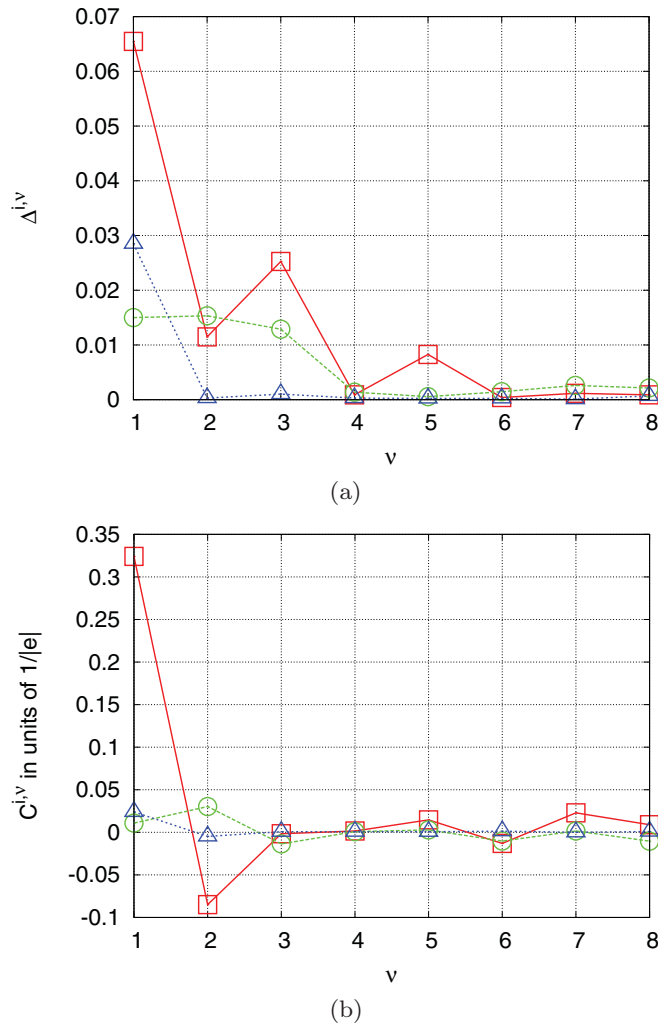


FIG. 5. (Color online) Differences in the occupations (a) and their charge derivatives (b) for $i = t_{2g}$ (\square), e_g (\circ), and p (\triangle) (see descriptions in the main text).

again, the important role of $\Delta^{t_{2g},1}$ for the magnetocrystalline anisotropy energy in these films.

Kittel illuminates his notion of the magnetocrystalline anisotropy energy (Sec. II C) by assuming for simplicity an infinitely large SOC, so an anisotropic atomic charge density is rigidly corotated with the magnetization (Fig. 1 of Ref. 18), and our Δ^i characterize the anisotropy of the charge density. In systems with finite (and often rather small) SOC this sketch is, of course, too rough for a quantitative description of E_{mca} . According to Eq. (1), what matters in such systems is the change of the electronic energies by SOC, especially for states with energies close to the Fermi energy ε_F . Figure 6(a) shows the spin-, atom-, and l_z -resolved scalar-relativistic electronic densities of states for the outermost layer of the nonrelaxed Fe film with $N_L = 15$. It is gratifying to see that the t_{2g} states that yield the largest $\Delta^{i,1}$ (relevant for Kittel's simplified view) have the largest density of states around ε_F (relevant for the more quantitative view). Figure 6(b) shows that also for the second-outermost atomic layer the density of states near ε_F is dominated by the t_{2g} states, so that their modifications by the SOC are probably most important for the magnetocrystalline

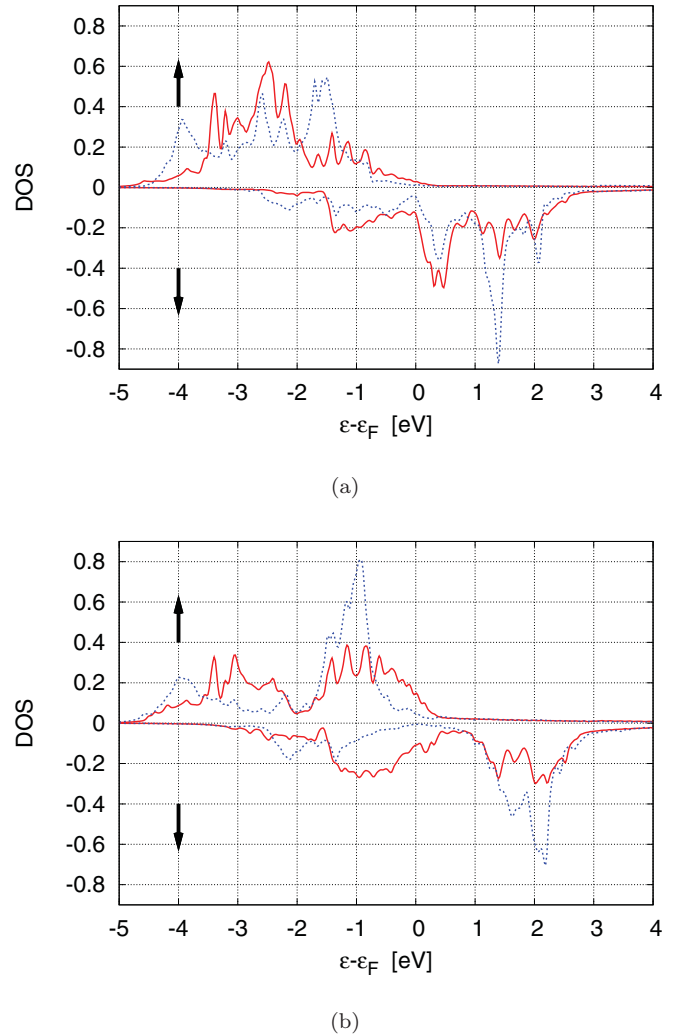


FIG. 6. (Color online) The spin-, atom-, and l_z -resolved electronic densities of states per eV of the scalar-relativistic calculation for the outermost (a) and the second-outermost (b) layer of the unrelaxed Fe film consisting of 15 atomic layers. The majority (minority) states are denoted by spin-up (spin-down). The full (dotted) lines represent the sum of the contributions of the three (two) t_{2g} (e_g) states, divided by 3 (2).

anisotropy energy E_{mca}^2 of this layer. Figure 5(a), however, shows, that the anisotropy of the orbital occupation numbers is much smaller for this layer, and therefore E_{mca}^2 is rather small (see Fig. 4).

D. Fe films on substrates

As mentioned in the Introduction, it is known that for simple ferromagnetic films the magnetoelectric effect is small, so very large fields are required to switch the magnetization from in-plane alignment to out-of-plane alignment. We confirm this for Fe films. We then show that it is possible to switch the magnetization direction already by small fields for very thin films grown on metallic substrates like Au.

The total magnetic anisotropy that determines the orientation of the magnetization usually is the sum of the magnetocrystalline anisotropy and the dipolar shape anisotropy. We calculated the shape anisotropy energy E_{sa} by use of the

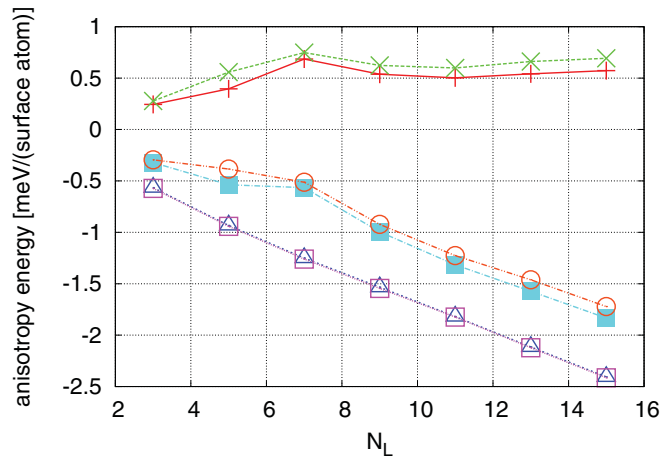


FIG. 7. (Color online) The various magnetic anisotropy energies E_{mca} , E_{sa} , and E_{ta} (see text) and their sum for neutral ($\Delta q = 0$) and charged [$\Delta q = 0.053 |e|/(\text{surface atom})$] Fe films as functions of the film thickness. $E_{mca}(\Delta q = 0)$ \circ , $E_{mca}[\Delta q = 0.053 |e|/(\text{surface atom})]$ \times , $E_{sa}(\Delta q = 0)$ \square , $E_{sa}[\Delta q = 0.053 |e|/(\text{surface atom})]$ \triangle , $E_{ta}(\Delta q = 0)$ \blacksquare , $E_{ta}[\Delta q = 0.053 |e|/(\text{surface atom})]$ \circ .

method described in Ref. 17 by calculating the dipole-dipole interaction energy between the atomic magnetic moments that we define by integrating the *ab initio* calculated spin-magnetization density over the muffin-tin spheres around the atomic positions. Thereby, there is only a very small magnetoelectric effect on the atomic magnetic moments (see also Refs. 11 and 31). For instance, when changing the number of electrons of the film by $\Delta N_{el}/(\text{surface atom})$ the magnitude of the moment of the surface atom changes linearly with ΔN_{el} , going from $2.963 \mu_B$ for $\Delta N_{el} = 0$ to $2.99 \mu_B$ for $\Delta N_{el} = -0.05$. Therefore, the magnetoelectric effect on E_{sa} is much smaller than the one on E_{mca} .

Figure 7 shows E_{mca} , E_{sa} and the total magnetic anisotropy $E_{ta} = E_{mca} + E_{sa}$ for the Fe (001) films as function of the number N_L of the atom layers for $\Delta q = 0$ and $\Delta q = 0.053$ electrons/(surface atom). [Please note that in the energy resolution of Fig. 7 the curves that represent the E_{sa} for different Δq (empty squares and triangles) coincide.] The magnetocrystalline anisotropy prefers an out-of-plane orientation of the magnetization and the shape anisotropy an in-plane orientation. The out-of-plane E_{mca} increases for positive Δq , but E_{ta} is negative for $\Delta q = 0$ and for the rather large value of $\Delta q = 0.053$ electrons/(surface atom) that corresponds to a large electric field of 1.166 V/\AA . This means that the magnetization of these films cannot be switched by application of reasonably large electric fields. In principle, the switching to the out-of-plane direction could be assisted by an additional large static out-of-plane magnetic field (see also Ref. 4), for instance, for $N_L = 5$ such a field of strength 0.6 T would enable us to switch the magnetization direction by a rather small electric field (leading to a small Δq).

We have performed the calculations also for Fe films on a Au substrate. Experimentally, a bcc Fe film can be grown epitaxially on a fcc Au substrate with nearly no lateral distortions in the Fe film. Thereby, the cubic unit cells of the bcc film are rotated in the plane of the interface by 45° with respect to the cubic unit cells of the Au substrate. In our

TABLE I. The values of E_{mca} , E_{sa} , and E_{ta} [all in meV/(surface atom)] for the two uncharged systems.

	E_{mca}	E_{sa}	E_{ta}
$\text{Fe}_2\text{-Au}_7\text{-Fe}_2$	1.593	-0.329	1.264
$\text{Fe}_3\text{-Au}_7\text{-Fe}_3$	0.073	-0.502	-0.429

calculation we model this situation in the following way. The Au substrate consists of seven infinitely extended fcc (001) Au layers, and the Au atoms are in the positions they would have if they were part of fcc bulk Au. Both surfaces of the Au substrate are covered by two ($\text{Fe}_2\text{-Au}_7\text{-Fe}_2$) or three ($\text{Fe}_3\text{-Au}_7\text{-Fe}_3$) infinitely extended bcc (001) layers, which are rotated with respect to the Au substrate in the above discussed way and that have an interlayer distance of $a_{bcc}/2 = a_{fcc}/(2\sqrt{2})$ (where a_{fcc} and a_{bcc} denote the cubic lattice constants of the fcc and bcc system) as long as the vertical positions of the Fe atoms are not relaxed. In our calculations we have relaxed these vertical positions of the Fe atoms. Thus, the Fe layers form a continuation of the fcc stacking of the Au substrate with modified, i.e., relaxed, layer distances. Please note that we do not have a multilayer system but a “trilayer” Fe-Au-Fe because the supercells are periodically repeated only in the lateral dimensions. The values of E_{mca} , E_{sa} , and E_{ta} for the uncharged systems ($\text{Fe}_2\text{-Au}_7\text{-Fe}_2$) and ($\text{Fe}_3\text{-Au}_7\text{-Fe}_3$) are given in Table I.

As discussed in Sec. III B, there is no direct contribution of the Au atoms to E_{mca} but an indirect contribution resulting from the large modifications of the shape of the wave functions at neighboring Fe atoms. The difference between the system with two or three Fe cover layers shows that this effect is not restricted to the Fe layer that is closest to the Au substrate, but there is a change in the wave functions and hence a modification of the atomic charge densities also in further distant Fe layers.

As explained in Sec. III A, the experimentally produced epitaxial Fe films do not necessarily have film thicknesses that correspond to integer numbers of atom layers. By linear interpolation between our data for two and three Fe layers we find that at a critical thickness corresponding to 2.75 atom layers there would be a transition between the in-plane and out-of-plane orientation of the magnetization. In Ref. 32 it was found experimentally that for Fe grown on Au(001) at 100 K, the easy axis of the magnetization is out of plane for films thinner than 2.8 atom layers and in plane for thicker films. When using a system close to the critical thickness, a switching of the magnetization direction can be achieved by application of rather small electric fields.

IV. CONCLUSIONS

In the present paper the physics of the magnetoelectric effect resulting from the electric-field-induced spin-dependent electron polarization is discussed. To do this, *ab initio* calculations within the spin-density functional electron theory are performed.

A method for the definition of layer-resolved contributions to the magnetoelectric effect on the magnetocrystalline anisotropy energy E_{mca} is introduced, which is based on the

very often used magnetic force theorem for the calculation of the E_{mca} . It is shown by the general theoretical arguments that this method is not strictly valid and, therefore, that the sum of the so-defined layer-resolved contributions in general is not identical to the *ab initio* calculated E_{mca} for the whole system. Nevertheless, it is shown numerically that at least for our considered systems the method is rather accurate. The knowledge of layer-resolved contributions to E_{mca} and their modifications by electric field is very helpful for a modeling of the magnetoelectric effects on the atomic level in systems, which are structurally too complicated for a complete *ab initio* treatment.

The physics of the magnetoelectric effect is analyzed in the spirit of Kittel's explanation of E_{mca} , in which the covalent bond energy related to the anisotropic charge density plays an important role. Quantities that characterize this anisotropic electron charge density and its magnetoelectric modification are introduced. Our numerical results show that these quantities are indeed helpful for the interpretation of the

magnetoelectric effects on E_{mca} . Finally, it is shown that in the heterosystem Fe-Au-Fe the magnetization direction can be switched between the in-plane and out-of-plane orientation by rather small fields, if the average thicknesses of the ultrathin Fe films have values close to a critical value. This is in contrast to the general opinion that a magnetoelectric manipulation of purely metallic systems requires extremely high electric fields, and this may suggest a new class of systems that can be used for special technological magnetoelectric devices.

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