Multiferroic heterostructures for spin filter applications: An *ab initio* study

Stephan Borek,[1] Jürgen Braun,[1] Hubert Ebert,[1] and Ján Minár[1,2]
[1]*Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstraße 5-13, 81377 München, Germany*
[2]*New Technologies-Research Centre, University of West Bohemia, Univerzitni 8, 306 14 Pilsen, Czech Republic*
(Received 24 July 2015; revised manuscript received 13 October 2015; published 9 November 2015)

Novel imaging spin-filter techniques, which are based on low-energy electron diffraction, are currently of high scientific interest. To improve the spin-detection efficiency a variety of new materials have been introduced in recent years. A new class of promising spin-filter materials are represented by multiferroic systems, as both magnetic and electric ordering exist in these materials. We have investigated Fe/$BaTiO_3$(001) for spin-filter applications, which is a prominent candidate due to its moderate spontaneous polarization of the $BaTiO_3$ substrate. Therefore we calculated diffraction patterns for spin polarized electrons incident on the Fe surface. Motivated by the fact that spin polarized low-energy electron diffraction is a surface sensitive method, we investigated the alterations of exchange and spin orbit scattering induced by switching the $BaTiO_3$ polarization. As shown by our studies the system obviously offers the possibility of realizing a multiferroic spin filter and manipulating the spin-orbit and exchange scattering by an external electric field. The calculations have been done for a large range of kinetic energies and polar angles of the diffracted electrons considering different numbers of Fe monolayers.

DOI: 10.1103/PhysRevB.92.174408 PACS number(s): 71.15.Mb, 75.70.Cn, 75.85.+t, 77.55.Nv

I. INTRODUCTION

Materials combining different ferroic properties are called multiferroics [1]. Multiferroic systems, especially multiferroic heterostructures, are promising in technical applications enabling the control of the magnetic moments of a ferromagnetic material by altering the electric polarization of a ferroelectric substrate or vice versa. The applications of such new systems are broad but, especially as memory devices, epitaxial thin films might be interesting [2]. The development of experimental techniques, such as the growing of epitaxial magnetic and ferroelectric materials, have been an essential requirement for the realization of multiferroic heterostructures [3,4]. Based on that it was possible to grow a well defined interface enabling an effective coupling between the participating ferroic phases. Thus various experimental groups investigated prototypical devices. Most of them used external electric fields to change the ferroelectric polarization. With that the influence on the magnetic properties of the ferromagnetic phase has been investigated [5].

To find suitable material combinations it is important to understand the coupling mechanism between both ferroic phases. Therefore different ferroelectric and ferromagnetic materials have been studied [6–9]. Within the various ferroelectric materials the perovskite $BaTiO_3$ (BTO) takes a prominent position due to its moderate spontaneous polarization at room temperature [7].

For the construction of a multichannel vector spin polarimeter at BESSY II several material types have been tested for the applicability as reflecting mirror for spin polarized electrons. Besides the well known materials W, Ir, and Fe the system Fe/BTO yielded interesting properties for spin-filter purposes. Especially, the predicted enhancement of the magnetic moments at the Fe overlayer give rise to an application as a spin filter based on exchange scattering [8]. Another feature is the dependence of the magnetic moments on the BTO polarization [8,10,11]. Here, the working principle could be based on altering the electric polarization of the BTO, affecting the magnetic moments at the Fe surface. This enables an electric control of the exchange scattering without any external magnetic field. Also a mechanical control of the BTO polarization is conceivable.

In this work we studied the scattering of spin polarized electrons from the surface of the multiferroic heterostructure Fe/BTO. We calculated diffraction patterns visualizing the dependency of the scattered intensity on the polar angles and kinetic energies. In our scattering geometry the polarization of the electrons were oriented perpendicular to the scattering plane. Due to that, both exchange and spin-orbit scattering occur [12,13]. We investigated the so-called exchange and spin-orbit asymmetries as well as the effective reflectivity and the figure of merit (FOM). Additionally we investigated the layer dependence of the exchange and spin-orbit scattering. We applied our method to 1, 2, and 3 monolayer (ML) Fe/BTO because their electronic and magnetic structure has been investigated in detail in previous works [8,14]. For all systems the crystal structure was taken from previous investigations, providing a relaxed interface and surface [8]. This accounts for the fact that SPLEED (spin polarized low-energy electron diffraction) is very surface sensitive due to the low kinetic energies of the incident electrons. For the calculation of the electronic properties and the electron diffraction we applied a fully relativistic KKR (Korringa-Kohn-Rostoker) method (SPR-KKR) in the framework of spin-polarized density functional theory to account for effects based on exchange and spin-orbit interactions in one step [15,16].

The paper is organized as follows: In Sec. II we describe the application of the underlying SPLEED theory in the framework of the SPR-KKR method. In Sec. III we discuss our computational results concerning the electron diffraction. In Sec. IV we summarize our results.

II. THEORETICAL APPLICATION

We briefly introduce the theoretical method implemented in the SPR-KKR program package for the calculation of spin-polarized electron scattering from arbitrary surface systems. The SPLEED calculations are done using the layered-KKR method [17]. This method describes the scattering of spin polarized electrons from a stack of atomic layers representing

 ©2015 American Physical Society

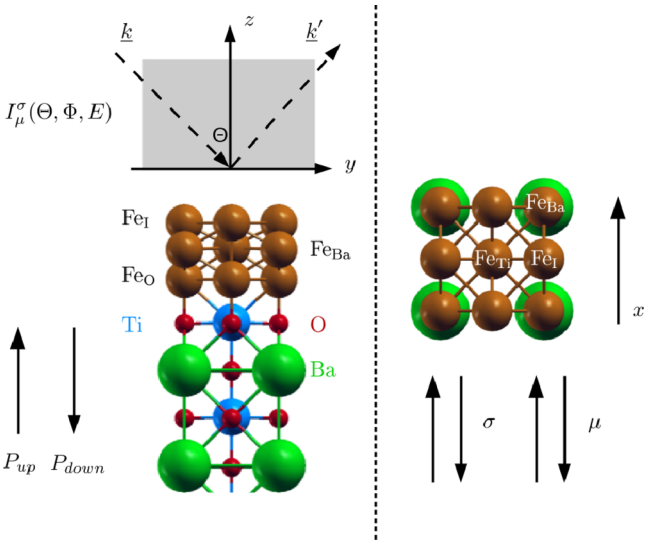

FIG. 1. (Color online) Half-space of 3 ML Fe/BTO used for the SPLEED calculations. Left: Side view. Right: Top view. The various atomic types have been indicated. The reflected electron intensity $[I^{\sigma}_{\mu}(\Theta,\Phi,E)]$ is drawn. Θ is the polar angle of the incident electrons. Additionally the parameters which have been varied are shown: The electric polarization of BTO ($P_{\rm up}$, $P_{\rm down}$), the polarization of the electron (σ), and the in-plane magnetization of the surface (μ). The scattering plane is spanned by the wave vectors ($\underline{k}$,$\underline{k}'$) and is aligned along the [010] direction. The polarization of the electron and the surface magnetization are altered along the [100] direction.

a semi-infinite surface system. Therefore one has to treat the multiple scattering within one specific atomic layer and the scattering between the atomic layers of the stack. The combination of both scattering mechanisms results in the calculation of the so-called bulk reflection matrix. With the bulk reflection matrix the diffraction of spin-polarized electrons from a surface is determined [12,17]. The scattering plane is spanned by the wave vector of the incident electron $\mathbf{k}$ and the scattered electron $\mathbf{k}'$ (see Fig. 1). In our calculations both surface magnetization and polarization of the electron were oriented perpendicular to that plane. Therefore exchange and spin-orbit scattering contribute [13]. The calculation of the scattered electron intensity was done for all combinations of magnetization and polarization; i.e.; one ends up with four different intensities (I^{σ}_{μ}) [12,13]. Here μ is the magnetization direction and σ gives the polarization direction of the electron. From the reflected intensities I^{σ}_{μ} the exchange asymmetry, spin-orbit asymmetry, and FOM are calculated. The spin-orbit asymmetry can be determined via the relation [12]

$$A_{\rm soc} = \tfrac{1}{2}(A_+ - A_-), \tag{1}$$

which can be ascribed to the reflected intensities using the definitions

$$A_+ = \frac{I^+_+ - I^-_+}{I^+_+ + I^-_+}, \tag{2}$$

$$A_- = \frac{I^+_- - I^-_-}{I^+_- + I^-_-}. \tag{3}$$

It is important to remark that the equations above define the exchange scattering for a specified magnetization direction.

The most important quantity for the characterization of the diffraction of electrons from a surface is the FOM. The reflectivity as well as the asymmetry (exchange or spin-orbit) contribute to this quantity. The FOM for both investigated magnetization directions can be calculated via

$$\mathrm{FOM}_{+(-)} = I_{+(-)}A^2_{+(-)}, \tag{4}$$

using the relations

$$I_{+(-)} = \tfrac{1}{2}(I^+_{+(-)} + I^-_{+(-)}). \tag{5}$$

This gives insight into changes of the scattering behavior by changing the magnetization direction at the surface. For the calculation of SPLEED patterns it is necessary to determine the single-site scattering matrices for the individual atomic types involved in the half-space of Fe/BTO. Therefore the self-consistent potentials necessary for the calculation of the single-site scattering matrices were taken from previous works [8,11]. Based on that, we were able to calculate the multiple scattering in the several atomic layers (Kambe X matrix) and the bulk reflection matrix.

Considering the escape of the diffracted electrons into the vacuum, one has to define the work function and the surface potential barrier. For the work function we applied 4.7 eV, which is a reasonable value for Fe(001), whereas the surface potential barrier was simulated by the Rundgren-Malmström parametrization [18,19]. We calculated SPLEED patterns for a broad range of kinetic energies and polar angles according to the working areas as scattering mirror. The calculations were done for the specular reflected beam and for the polarization of the BTO pointing in the direction of the surface normal ($P_{\rm up}$) and to the opposite direction ($P_{\rm down}$).

In Fig. 1 the side and top views of 3 ML Fe/BTO are shown. The unit cell of BTO corresponds to a tetragonal distorted structure ($P4mm$) with a lattice parameter of 3.943 Å [9].

Remarkably, the surface of the BTO has a (001) orientation and is terminated by O and Ti. Detailed studies of the termination of the Fe/BTO system have been done in previous experimental and theoretical investigations [8,10,11,14]. In our calculations the multiferroic heterostructure was simulated by a half-space of four unit cells of BTO. The half-space potentials reflect the relaxation of the electronic structure going from the bulk to the surface region. Atomic types which are located below the fourth unit cell have been treated as bulk-like. Due to the distorted structure of the unit cell of BTO ($P4mmm$) at room temperature a remanent electrical polarization occurs. The polarization originates from a shift of the Ti and O atoms in opposite directions in combination with a distortion of the unit cell [20].

The composition of the interface has been investigated in previous works [8,10]. Here we briefly summarize the main structural data. The first Fe layer (Fe_O) is on top of the O atoms. The second Fe layer has two inequivalent Fe sites which are on top of Ti (Fe_{Ti}) and Ba (Fe_{Ba}). The third Fe layer (Fe_I) is placed on top of the Fe atoms of the first Fe layer [8]. The crystal structure of the surface and the interface have been relaxed using the Vienna Ab initio Simulation Package (VASP) [21,22]. Based on the relaxed crystal structure, we applied the fully relativistic multiple scattering formalism for the calculation

of the SPLEED patterns as sketched above [16]. The self-consistent calculation of the atomic potentials has been done previously using a multicode approach [11,23,24].

III. RESULTS AND DISCUSSION

The results of the electronic structure calculations, especially the spin magnetic moments, are in good agreement with published data [8,11]. The magnetic properties of the Fe surface are essential for the exchange scattering of the spin-polarized electrons. Changing the polarization of the BTO affects the magnetic moments of the Fe layers. The surface magnetic moments react on a competition of the reduced number of nearest neighbors at the surface and hybridization effects between the Fe $3d$ and O $2p$ states as well as the Fe $3d$ and Ti $3d$ states [6–8]. It was shown that for 1 ML Fe/BTO a ferromagnetic ground state occurs with large spin magnetic moments for Fe due to the reduced coordination number at the surface. For 2 ML Fe/BTO a ferrimagnetic ground state was predicted; i.e., the Fe atoms in the second Fe layer (Fe_{Ti}, Fe_{Ba}) have an antiparallel alignment of their spin directions and different magnetic moments. For 3 ML Fe a ferromagnetic ground state is restored. The magnetoelectric coupling is based on hybridization effects [8]. It has been shown that a change of the BTO polarization affects the spin magnetic moments of Fe by changing the hybridization of the Fe, Ti, and O states. A smaller (larger) hybridization of the Fe $3d$ states with the Ti $3d$ states and O $2p$ states results in a larger (smaller) spin magnetic moment of Fe [11]. The change of the magnetic properties affects the optical properties as has been shown for the absorptive part of the conductivity tensor [11]. Additionally the magnetic properties are detectable using the scattering of electrons with low kinetic energy, as will be shown below.

In Fig. 2 the reflectivity for 3 ML Fe/BTO for a [100] surface magnetization is shown.

The ranges of polar angles and kinetic energies have been chosen according to a possible application as scattering mirror [25]. Referring to the kinetic energy, the diffraction patterns can be divided into two main parts marked by the emergence threshold. The emergence threshold marks the occurrence of a new diffracted beam and is located around a kinetic energy of 8 eV. This new diffracted beam lowers the intensity of the specular diffracted one and reduces the intensity in the diffraction pattern.

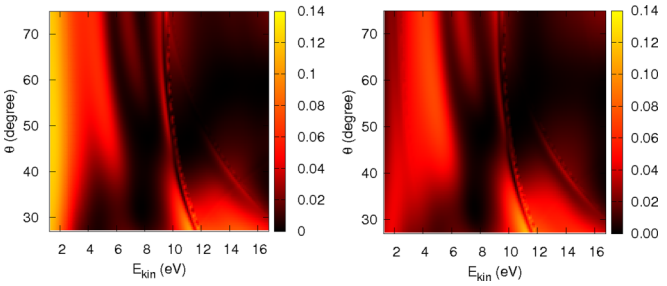

FIG. 2. (Color online) Diffraction pattern of the reflectivity for 3 ML Fe/BTO for a [100] orientation of the magnetization direction. Left: The polarization of the BTO is directed along the surface normal (P_{up}). Right: The polarization of the BTO is directed in opposite direction (P_{down}).

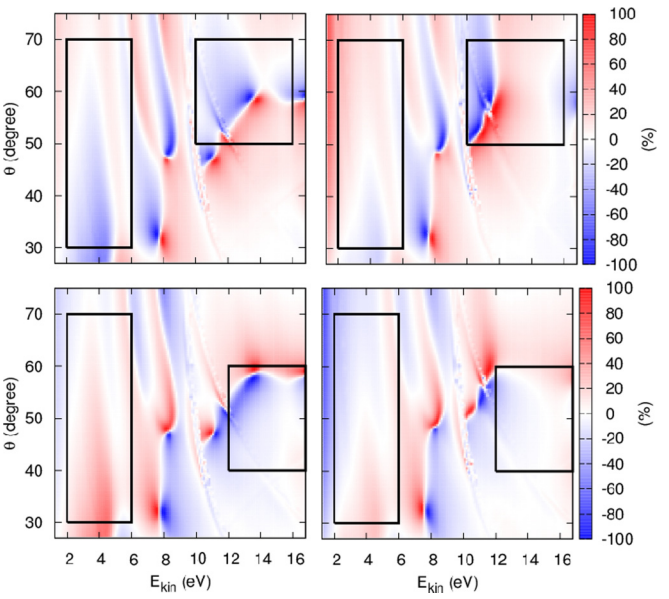

FIG. 3. (Color online) Top panel: Diffraction pattern of the exchange asymmetry (A_+) for 3 ML Fe/BTO. The magnetization of the surface is along the [100] direction. Left: The polarization of the BTO is directed along the surface normal (P_{up}). Right: The polarization of the BTO is directed in opposite direction (P_{down}). Bottom panel: Diffraction pattern of the exchange asymmetry (A_-) for 3 ML Fe/BTO. The magnetization of the surface is along the [$\bar{1}$00] direction. Left: The polarization of the BTO is directed along the surface normal (P_{up}). Right: The polarization of the BTO is directed in opposite direction (P_{down}).

The highest values for the reflectivity occur for low kinetic energies (≈4 eV) and cover nearly the total range of polar angles. This is important for a later application, as the scattering mirror giving the possibility to vary the sample position with respect to the polar angles. In the energy range lower (higher) than the emergence threshold a large (small) sensitivity due to a change of the BTO polarization is visible. This is due to the fact that electrons with lower kinetic energies react more sensitively to changes of the surface magnetization, i.e., concerning variations of the exchange scattering. A area with high reflectivity is visible for kinetic energies above 10 eV and polar angles of 30°. This area reacts less sensitively to a change of the BTO polarization. Again this can be attributed to the higher kinetic energy of the diffracted electrons making them less sensitive to changes in the exchange scattering.

In Fig. 3 (top panel) the exchange asymmetries for 3 ML Fe/BTO are shown for both BTO polarizations. The color scheme in the diffraction patterns indicates a change of the alignment of electron polarization and surface magnetization. The red color corresponds to a parallel alignment of polarization and magnetization, and the blue color corresponds to an antiparallel alignment. The magnetization direction was oriented along the [100] direction (top panel). For the investigated range of polar angles and kinetic energies two areas (marked by black rectangles) occur with a large variation of the exchange scattering.

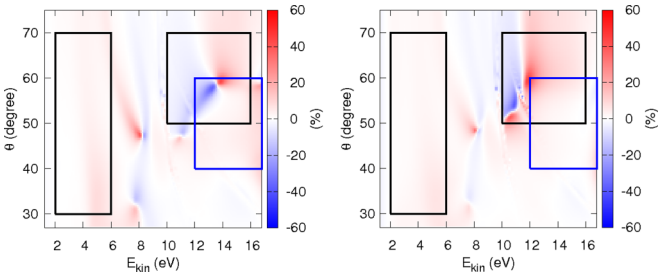

FIG. 4. (Color online) Diffraction pattern of the spin-orbit asymmetry (A_{soc}) for 3 ML Fe/BTO. Left: The polarization of the BTO is directed along the surface normal (P_{up}). Right: The polarization of the BTO is directed in opposite direction (P_{down}).

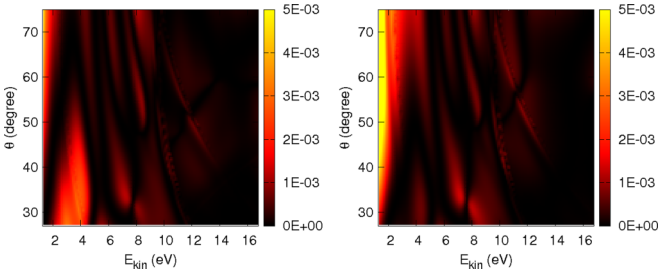

FIG. 5. (Color online) Diffraction pattern of the FOM for a [100] orientation of the magnetization direction for 3 ML Fe/BTO. Left: The polarization of the BTO is directed along the surface normal (P_{up}). Right: The polarization of the BTO is directed in opposite direction (P_{down}).

The first area is located at lower kinetic energies of the incident electrons ($\leqslant$6 eV) the second area at higher kinetic energies (12–17 eV). An altering of the BTO polarization from P_{up} to P_{down} changes the reflected spin polarization in the marked areas. Especially for the area at low kinetic energy and high polar angle, which provides high reflectivity, a change of the reflected spin direction is visible.

In addition the exchange scattering for a magnetization in [$\bar{1}$00] direction is shown in Fig. 3 (bottom panel), again for both polarization directions of the BTO. In comparison to a magnetization pointing along the [100] direction, a less pronounced change in the exchange scattering occurs, especially for higher kinetic energies. This has to be attributed to the spin-orbit scattering caused by the fact that for a scattering configuration with vanishing spin-orbit interaction $A_+ = -A_-$ holds [13].

The spin-orbit induced contribution to the specular scattering of the electrons is shown in Fig. 4. The different colors of the rectangles indicate areas with higher (black) and lower (blue) sensitivity to a change of the BTO polarization. These areas coincide with the rectangles in Fig. 3. The areas marked by blue rectangles are less sensitive to a change of the BTO polarization. They correspond to the areas drawn in Fig. 3 (bottom panel) with a magnetization pointing in [$\bar{1}$00] direction. In summary, a large (small) change of the spin-orbit asymmetry coincides with a large (small) change of the exchange asymmetry. The important information on using the multiferroic heterostructure as spin polarizing mirror is the enhanced sensitivity of exchange and spin-orbit asymmetry for a [100] orientation of the magnetization. Therefore an application of the system would be preferred with a [100] magnetization direction.

In Fig. 5 the FOM for 3 ML Fe/BTO is shown. The FOM was calculated for both BTO polarization directions. Due to Eq. (4) the FOM scales linearly with the reflectivity, whereas the exchange asymmetry enters to the power of 2, therefore dominating the result. Because of that the areas of a high FOM coincide with the areas of a high exchange scattering. The FOM has significant changes for kinetic energies $\leqslant$6 eV. Therefore an application of 3 ML Fe/BTO would be most promising for SPVLEED (spin-polarized very-low-energy electron diffraction) experiments.

Around 4 eV a high FOM for a P_{up}-oriented BTO polarization is visible. Changing the BTO polarization to P_{down} results in a strong decrease. Compared with the exchange asymmetry it is visible that mainly electrons with an antiparallel alignment of magnetization and electron polarization are affected. For these electrons the system of 3 ML Fe/BTO could serve as a kind of valve using the change of the BTO polarization. In that sense a BTO polarization pointing to the surface (P_{up}) keeps electrons with defined spin direction passing. Switching the BTO polarization to the opposite direction results in a drop of the FOM, i.e., no electrons can pass the spin filter.

Compared to the well known spin filter Fe(001)-$p(1\times1)$-O the reflectivity is in the same order of magnitude [25,26]. However, the FOM is an order of magnitude lower for the 3 ML Fe/BTO, lowering its applicability as spin-polarizing mirror. It is know that Fe(001)-$p(1\times1)$-O has a longer lifetime in vacuum and a higher FOM [27] in comparison to a Fe(001) surface. Therefore it would be interesting to investigate how an O overlayer on top of Fe/BTO affects the exchange scattering.

Layer dependence of SPLEED

In addition we investigated the electron scattering for 1 ML and 2 ML Fe/BTO. The structural properties correspond to the systems studied in previous works [8]. Comparing the exchange asymmetry of 1 ML, 2 ML, and 3 ML Fe/BTO, the highest sensitivity for a change of the BTO polarization results for 3 ML Fe/BTO. Therefore the results for 1 ML and 2 ML will not be shown in detail here. Nevertheless, the scattering patterns for 1 ML and 2 ML reveal differences by changing the BTO polarization for the same areas as for 3 ML Fe/BTO. Of course, the differences in the exchange scattering comparing 1 ML, 2ML, and 3 ML Fe/BTO lead back to the in-plane spin magnetic moments and their reaction to a change of the BTO polarization. The changes of the spin magnetic moments due to a change of the BTO polarization are listed in Table I. The

TABLE I. Layer resolved change of the in plane spin magnetic moments [$\Delta m_s = m_s(P_{up}) - m_s(P_{down})$] by changing the polarization of BTO. Magnetization points along the [100] direction. Units are given in μ_B.

	1 ML	2 ML	3 ML
Fe_I			−0.18
$Fe_{Ti} + Fe_{Ba}$		−0.08	0.04
Fe_O	−0.02	0.0	0.2

largest alteration occurs for the topmost Fe layer for 3 ML Fe/BTO. Provided that an incident electron interacts mainly with the topmost Fe layer, one will see the largest change of the magnetic moment for 3 ML Fe/BTO. Due to that, the most pronounced differences of the exchange scattering can be expected for this system. For 1 ML and 2 ML Fe/BTO the changes are smaller, resulting in less pronounced changes of the diffraction patterns.

IV. SUMMARY

Using an *ab initio* formalism we calculated SPLEED patterns for 1, 2, and 3 ML Fe/BTO. We investigated the change of the reflectivity, the FOM, and both exchange and spin-orbit asymmetry by changing the polarization of the BTO. We showed that one can expect the largest changes of the diffraction patterns for 3 ML Fe/BTO. We located two areas in the diffraction patterns for which a change of the BTO polarization induces a significant change of the exchange asymmetry. Therefore a combination of a ferroelectric and a ferromagnetic material would enable new applications for spin-filter purposes, according to the working areas, especially for VSPLEED experiments. For higher kinetic energies the Fe/BTO system has a smaller FOM compared to the intensively studied Fe(001)-$p(1\times1)$-O surface. Therefore we want to investigate the impact of an additional O layer on top of Fe/BTO in the near future.

ACKNOWLEDGMENTS

We thank the BMBF (05K13WMA), the DFG (FOR 1346), CENTEM PLUS (LO1402), CENTEM (CZ.1.05/2.1.00/03.0088) and the COST Action MP 1306 for financial support.

[1] H. Schmidt, Ferroelectrics **162**, 317 (1994).
[2] C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science **303**, 488 (2004).
[3] M. Dawber, K. M. Rabe, and J. F. Scott, Rev. Mod. Phys. **77**, 1083 (2005).
[4] H. Zheng *et al.*, Science **303**, 661 (2004).
[5] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[6] C.-G. Duan, R. F. Sabirianov, W.-N. Mei, S. S. Jaswal, and E. Y. Tsymbal, Nano Lett. **6**, 483 (2006).
[7] M. Fechner, S. Ostanin, and I. Mertig, Phys. Rev. B **77**, 094112 (2008).
[8] M. Fechner, I. V. Maznichenko, S. Ostanin, A. Ernst, J. Henk, P. Bruno, and I. Mertig, Phys. Rev. B **78**, 212406 (2008).
[9] M. Fechner, S. Ostanin, and I. Mertig, Phys. Rev. B **80**, 094405 (2009).
[10] C.-G. Duan, S. S. Jaswal, and E. Y. Tsymbal, Phys. Rev. Lett. **97**, 047201 (2006).
[11] St. Borek, I. V. Maznichenko, G. Fischer, W. Hergert, I. Mertig, A. Ernst, S. Ostanin, and A. Chassé, Phys. Rev. B **85**, 134432 (2012).
[12] R. Feder, J. Phys. C: Solid State Phys. **14**, 2049 (1981).
[13] E. Tamura, B. Ackermann, and R. Feder, J. Phys. C: Solid State Phys. **17**, 5455 (1984).
[14] H. L. Meyerheim, F. Klimenta, A. Ernst, K. Mohseni, S. Ostanin, M. Fechner, S. Parihar, I. V. Maznichenko, I. Mertig, and J. Kirschner, Phys. Rev. Lett. **106**, 087203 (2011).
[15] H. Ebert, D. Ködderitzsch, and J. Minár, Rep. Prog. Phys. **74**, 096501 (2011).
[16] H. Ebert *et al.*, The Munich SPR-KKR package, version 6.3, http://olymp.cup.uni-muenchen.de/ak/ebert/ SPRKKR, 2012.
[17] R. Feder, *Polarized Electrons in Surface Physics* (World Scientific, Singapore, 1985).
[18] H. L. Skriver and N. M. Rosengaard, Phys. Rev. B **45**, 9410 (1992).
[19] J. Rundgren and G. Malmström, J. Phys. C: Solid State Phys. **10**, 4671 (1977).
[20] A. Chassé, St. Borek, K.-M. Schindler, M. Trautmann, M. Huth, F. Steudel, L. Makhova, J. Gräfe, and R. Denecke, Phys. Rev. B **84**, 195135 (2011).
[21] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[22] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[23] M. Lüders, A. Ernst, W. M. Temmerman, Z. Szotek, and P. J. Durham, J. Phys.: Condens. Matter **13**, 8587 (2001).
[24] H. Ebert, Rep. Prog. Phys. **59**, 1665 (1996).
[25] C. Thiede, C. Langenkämper, K. Shirai, A. B. Schmidt, T. Okuda, and M. Donath, Phys. Rev. Appl. **1**, 054003 (2014).
[26] S. Borek, J. Braun, J. Minár, and H. Ebert, Phys. Rev. B **92**, 075126 (2015).
[27] R. Bertacco, D. Onofrio, and F. Ciccacci, Rev. Sci. Instrum. **70**, 3572 (1999).