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Calculation of the interface exchange coupling constants between Fe and FeF₂-like fluorides[☆]

Mariana Weissmann^a, Ana María Llois^a, Miguel Kiwi^{b,*},¹

^aDepartamento de Física, Comisión Nacional de Energía Atómica, Avda. del Libertador 8250, (1429) Buenos Aires, Argentina

^bFacultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, 6904411, Chile

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Abstract

The interface exchange coupling between ferromagnetic (F) and antiferromagnetic (AF) materials is interesting in itself and has also attracted recent attention in relation to the exchange bias phenomenon. A major difficulty in developing a reliable exchange bias theory lies in the fact that both the F and AF interface characteristics (geometry and physical parameters) are hard to determine experimentally and complicated to estimate theoretically. We adopt in this paper two alternative interface configurations to obtain upper and lower bounds for the computed values of the exchange coupling across the interface between metallic Fe and insulating FeF₂, derived on the basis of ab initio calculations implemented for a periodic supercell. Electronic structures and total energies were computed within density functional theory using the generalized gradient approximation for the exchange correlation potential. We expect the results obtained to be useful in model simulations with larger unit cells and non-collinear spins. © 2001 Published by Elsevier Science B.V.

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1. Introduction

The interface between two different solids is of major importance to properly describe and understand a large variety of systems. Moreover, its properties are interesting both from a basic physics point of view, as well as to comprehend the

operation of many electronic devices [1,2]. However, interfaces are difficult to characterize experimentally since only recently it is feasible to design and implement interface specific probes [3]. From a theoretical point of view the situation is not less complicated; the characteristics of a solid, as for instance crystal and electronic structure, change significantly in the vicinity of the interface. Thus, lattice mismatch and reconstruction, charge transfer and other phenomena have to be incorporated to elaborate a proper description.

One particular property that is interface dominated is the exchange bias (EB) phenomenon, that

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*Corresponding author.

E-mail address: mkiwi@puc.cl (M. Kiwi).

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has attracted renewed attention during the last years [1]. The characteristic signature of EB is the shift of the center of the magnetic hysteresis loop from its normal position at $H = 0$ to a different position at $H_E \neq 0$. It occurs in systems [1] composed by an antiferromagnet (AF) that is in atomic contact with a ferromagnet (F) if the sample is either grown or cooled below the respective Néel and Curie temperatures, in an external cooling field. While the study of EB is interesting in itself, much of the present excitement is related to its application in the technology of magnetic sensors and as stabilizers in magnetic reading heads [2]. During the nearly 50 years since its discovery [4,5] it has become evident that EB is an interface driven phenomenon [6–8], which makes the study of these interfaces a necessary requirement to develop a satisfactory understanding of the phenomenon [9,10].

The systems which exhibit EB are many and varied [1]: thin films, single crystal antiferromagnets with metallic coating, polycrystalline and amorphous ferromagnets in contact with ordered and disordered AF oxides and salts. In addition, the magnetic structure in the vicinity of the interface is not necessarily identical to the bulk magnetic ordering. The above obstacles are added to the complexity of the magnetic structure, with many equivalent easy axes directions often present.

Well aware of all the difficulties to attack this problem [11], which were sketched above, we nevertheless implement in this contribution a method to estimate the magnitude of the exchange parameters in the vicinity of the F/AF interface. To achieve this goal the electronic structures and total energies of the model system are calculated for different collinear magnetic configurations. This is done within density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange correlation potential. On the basis of this model we obtain approximate, but reliable, estimates for the exchange parameters of the system under study.

Previous calculations [9,12] have looked for the possibility of non-collinear magnetic structures at F/AF interfaces, as a function of the unknown exchange parameters. However, experimental re-

sults for comparison only became available during the last year, when the direct observation of the microscopic spin structure on both sides of the interfaces was achieved [10,13]. Also recently non-collinearity has been incorporated into ab initio codes, and some simple unit cells have already been studied with this technique [14,15]. The aim of this contribution is, in some sense, to connect these two approaches, since it provides exchange parameters extracted from ab initio calculations that can be used as inputs for Monte Carlo simulations in conjunction with a Heisenberg model. This way one has the advantage that much larger unit cells than in ab initio calculations can be treated.

This paper is organized as follows: after the introduction the method is presented in Section 2 and its results are given in Section 3. Finally, in Section 4 the results are analyzed and conclusions are drawn.

2. Method of calculation

As mentioned before, to a large extent the atomic arrangement and coordination at the interface has to be modeled by educated guesswork. The large lattice mismatch present in the systems studied in this work inevitably gives rise to a rather irregular interface structure [3,16] and consequently theoretical models should focus on characteristics that are shared by different structures. Periodic systems, with a relatively small supercell size, are the only ones amenable to the kind of ab initio calculations that we performed. For them, electronic band structures and total energies were calculated within the DFT, using the GGA of Perdew, Burke and Ernzerhof (PBE–GGA) for the exchange correlation potential. We employed the spin polarized full potential linearized plane wave (FP-LAPW) method with the WIEN97 code [17]. Energy convergence better than 10^{-3} eV/atom was achieved with the plane wave cutoff set at 14 Ry and with the required number of k -points in the reciprocal unit cell.

The exchange interaction parameters $J_{i,j}$ were estimated by fitting the calculated total energies per unit cell, for different magnetic structures, to

the simplest Ising model

$$E^{\text{Ising}} = - \sum_{\langle i,j \rangle} J_{i,j} S_i S_j, \quad (1)$$

where the indices i and j label the atoms and the summation incorporates neighbors up to a certain distance that will be defined below. The number of $J_{i,j}$'s that are feasible to estimate depends on the number of different magnetic structures that can be stabilized in the self consistent calculations, while limiting the unit cell to a reasonable size [18,19].

3. Results

3.1. Bulk transition metal fluorides of rutile structure

In order to confirm that the method described above is accurate enough to yield reliable values of the exchange parameters, several transition metal fluorides, that crystallize in the rutile structure, were investigated. The electronic structure of the family of ionic insulator compounds MF_2 ($M = \text{Mn, Fe, Co}$ and Ni) was calculated, for the experimentally determined lattice parameters, in the F and AF configurations. The tetragonal rutile structure of these compounds can be characterized as follows [20–22]: the metal atoms M are located at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the F at $(1 \pm x, 1 \pm x, 0)$ and $(\frac{1}{2} \pm x, \frac{1}{2} \mp x, \frac{1}{2})$ with $x = 0.305$ as illustrated in Fig. 1. All these systems are AF, and the M atom

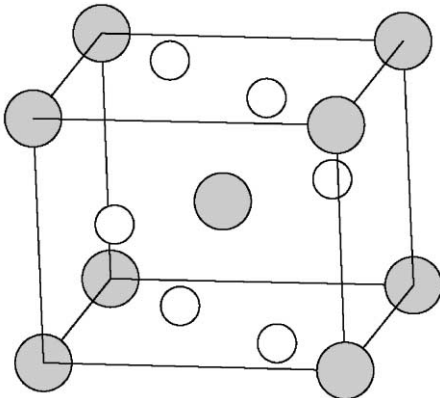


Fig. 1. Unit cell of the rutile structure MF_2 . Large circles represent the metal atoms M , small ones the F atoms.

at the cell center (Fe2) has opposite spin relative to the corner atoms (Fe1). These Fe atoms are equivalent in the bulk material, but they are not equivalent in the $(1\ 1\ 0)$ surface, as Fe2 loses one of its F nearest neighbors. In relation to their magnetic configurations these systems have been described either by Heisenberg or Ising Hamiltonians [18,22].

If the computations are restricted to one unit cell, with two formula units, only the largest magnetic coupling constant can be evaluated, i.e. that between neighbors along the $(1\ 1\ 1)$ direction. It should be noticed that the largest J value does not couple the nearest neighbor metal atoms, which lie along the $(0\ 0\ 1)$ axis, but the next nearest neighbor ones. The first neighbor exchange coupling constant is much smaller and it can be estimated by calculating the total energy of a larger unit cell [18]. For convergence 500 k -points in the reciprocal unit cell are required.

The exchange interaction energy ΔE_{12} , between Fe1 and Fe2 in Fig. 1, is given by the energy difference between the total energies of the F and AF configurations. It can be written as

$$\Delta E_{12} = 16J_{12}S^2, \quad (2)$$

since there are 8 atoms of Fe2 type surrounding each one of Fe1 type, all of them with nominal atomic spin $S = 2$. Our results for the numerical implementation of the model outlined above, as well as those of Ref. [18] (obtained by Hartree–Fock calculations) and the corresponding experimental results, are given in Table 1. As expected, Hartree–Fock and GGA approximations underestimate and overestimate, respectively,

Table 1

Total energy differences per unit cell, two MF_2 formula units, in meV, between the ferro and antiferromagnetic structures for the transition metal fluorides calculated in this paper and in Ref. [18]. The corresponding coupling constants J , in meV, are compared with experimental values

	ΔE	ΔE (Ref. [18])	S	J	J (Ref. [18])	J (exp)
MnF_2	163	7.35	$\frac{5}{2}$	1.64	0.071	0.294
FeF_2	98	3.97	2	1.52	0.060	0.436
CoF_2	35	2.29	$\frac{3}{2}$	0.98	0.061	0.544
NiF_2	116	3.57	1	7.26	0.216	1.663

the coupling constants, while the converse applies to the energy gaps. Our calculations correctly describe the systems as AF insulators and they provide what we believe to be reasonable estimates for the magnetic coupling constants we are interested in.

2.1. Model superlattices and interfacial structures

From now on we focus our interest on Fe/FeF₂, whose magnetic properties are qualitatively very similar to other Fe/MF₂ systems. In addition, we limit our interest to the (110) compensated AF interface.

The Fe/FeF₂ interfaces are modeled in a supercell geometry as periodically repeated sequences of Fe and FeF₂ slabs. The FeF₂ slab is modeled as an ideal truncation of the lattice along the (110) crystal face of the corresponding bulk structure. As FeF₂ is significantly stiffer than pure Fe the experimental lattice parameters of FeF₂ were used. However, the misfit of the two bulk lattices is quite significant, so that to match the surface unit cells the Fe slab had to be distorted considerably. We

did this in two different ways: in one case by in-plane expansion and in the other by in-plane contraction, which we denote as BCT and FCT-like, respectively. Adopting these two extreme configurations, with either one or two bulk Fe atoms per metal atom of the fluoride surface, we intend to establish upper and lower bounds for the computed values of the exchange parameters. The Fe slab distortion preserves, in all the calculations, the density of bulk BCC iron. The interslab distance is obtained by minimizing the total energy of the superlattice, and the distance between Fe atoms, on both sides of the interface, results equal to 3.2 Å. This distance should be compared with the first neighbor distance of Fe atoms in bulk Fe, which is 2.5 Å, and in the rutile structure where it amounts to 3.7 Å.

As a first approximation we adopt a supercell consisting of one monolayer of FeF₂ (110) and three monolayers of Fe (001). Therefore the unit cell contains: in the BCT-like case (3 BCT) 8 Fe atoms and 4 F atoms and, in the FCT like case (3 FCT) 14 Fe atoms and 4 F atoms, as illustrated

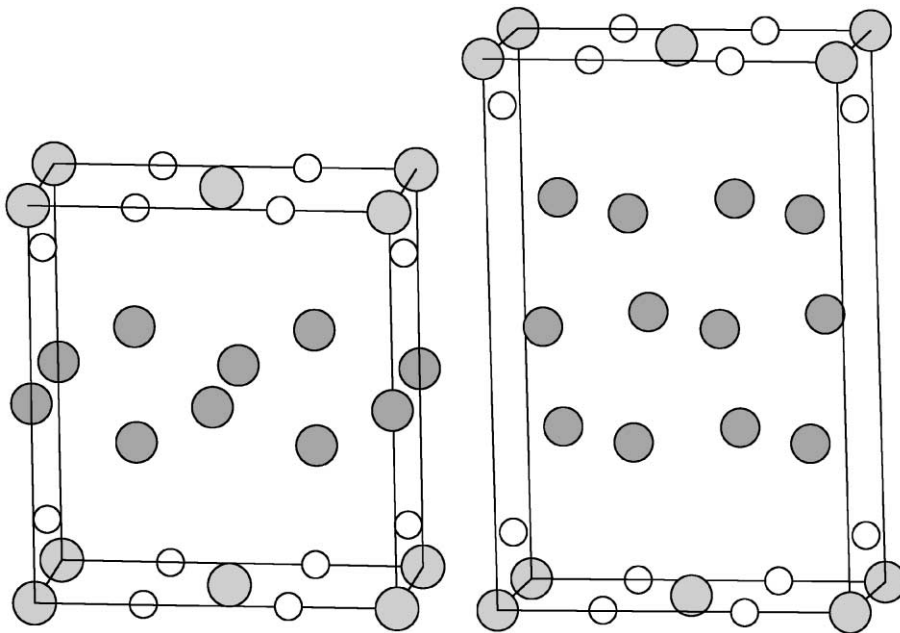


Fig. 2. Supercells used in the calculations. (a) 3 BCT (b) 3FCT. Large circles represent the Fe atoms, small ones the F atoms. The atoms on the vertices of the tetragonal cell are of Fe1-type, while the ones at the face center are Fe2-type. The three layers of bulk Fe atoms are the darker ones in the vicinity of the mid-height of the cell.

Table 2

Total energies per unit cell (in meV) of the model superlattices illustrated in Fig. 2 for the various magnetic configurations. F and AF indicate the orientation of the spin with respect to the external magnetic field. In each column the lowest energy state is taken as the zero of energy

Configuration	Fe1	Fe2	ΔE FCT	ΔE 3BCT	ΔE 5BCT
A	F	F	0	23	37
B	AF	AF	283	163	175
C	F	AF	141	44	80
D	AF	F	23	0	0

in Fig. 2. For the BCT-like case we also implemented the computation for five Fe (5BCT) monolayers and the results obtained differed from those of the three layer case within the accuracy of the whole calculation. The total energies are given in Table 2 for the different supercells in four magnetic configurations, denoted as A, B, C and D, which are all stable local minima. To build Table 2 it is assumed that the applied external magnetic field is strong enough to orient the spins in the Fe slab in a particular direction and therefore only the four possible spin orientations of the two metal atoms of the fluoride layer (Fe1 and Fe2 in Fig. 2) must be investigated. The magnetic moments, obtained by subtracting the two spin densities inside the corresponding muffin-tin spheres, are 3.1 and $3.5 \mu_B$ for Fe1 and Fe2, while the same calculation for bulk FeF_2 gives $3.6 \mu_B$. This implies that the Fe atoms of the fluoride monolayer are only slightly modified, with respect to bulk fluoride, by the presence of the Fe metal slab.

In order to implement the above described Ising type model the energy difference between any two of the magnetic configurations has been separated into three terms: the first describes the interaction between Fe1 and Fe2 (ΔE_{12}), the second and third the interaction between Fe1 and Fe2 with the whole Fe slab (ΔE_{1i}) and (ΔE_{2i}), respectively. Thus

$$E_A - E_B = \Delta E_{1i} + \Delta E_{2i}, \quad (3)$$

$$E_A - E_C = \Delta E_{12} + \Delta E_{2i}, \quad (4)$$

$$E_A - E_D = \Delta E_{12} + \Delta E_{1i}. \quad (5)$$

Solving this system of equations using the values given in Table 2 we obtain the following results: for BCT-like iron $\Delta E_{12} = +70$ meV, $\Delta E_{1i} = -48$ meV, $\Delta E_{2i} = -92$ meV. For FCT-like iron: $\Delta E_{12} = +60$ meV, $\Delta E_{1i} = -82$ meV, $\Delta E_{2i} = -200$ meV. The Fe1–Fe2 interaction is AF, and is smaller than in bulk fluoride (see Table 1) since metal atoms at the fluoride surface have a reduced number of F neighbors. On the other hand, the interaction between the fluoride iron atoms and the iron slab is of the opposite sign. The fact that the interfacial interaction is considerably larger for the FCT-like structure is of course due to the larger coordination of the interfacial Fe atoms. Regarding the difference between ΔE_{1i} and ΔE_{2i} , we notice that the presence of F mediating the interaction between two Fe atoms, as expected, weakens the strength of the ferromagnetic exchange coupling.

These energy differences should be expressed, as in Eq. (1), by sums over neighbors of the product of the spins times the corresponding exchange coupling constants. Not being able to estimate separately so many parameters we have assimilated all the unknowns into the three energies E_{12}, E_{1i}, E_{2i} . These energies play the role of effective coupling constants. Thus, as in Ref. [23], we have incorporated the magnitude of the different spins into the exchange constants J . In addition to that, our ΔE 's include the degeneracy of each type of neighbor atoms and for the case of the bulk metal they also include non-equivalent interactions.

4. Discussion and conclusions

When addressing the study of interface magnetic exchange coupling, the main unknown feature is the interface atomic structure, which implies that crucial assumptions on the atomic distribution in the neighborhood of the interface have to be made.

In this paper, total energy calculations were performed for several bulk fluorides in the rutile structure and provide reasonable estimates for the exchange coupling constants J . Thus, it seems quite likely that a correct description for the interface constants can be achieved, provided that

an adequate model for the interface atomic geometry is conjectured. Two extreme limiting cases of the Fe/FeF₂ system were explored, and they yield values of J that are quite close to each other and of the correct order of magnitude. Therefore, these should be useful in the study of interface dominated mechanisms, in particular, for numerical simulations of interface properties like the study of the exchange bias phenomenon.

References

- [1] J. Nogués, I.K. Schuller, *J. Magn. Magn. Mater.* 192 (1999) 203.
- [2] B. Dieny, V.S. Speriosu, S.S.P. Parkin, J.C. Scott, B.A. Gurney, D.R. Wilhoit, D. Mauri, *Phys. Rev. B* 43 (1991) 1297.
- [3] G. Charlton, P.B. Howes, C.A. Muryn, H. Raza, N. Jones, J.S.G. Taylor, C. Norris, R. McGrath, D. Norman, T.S. Turner, G. Thornton, *Phys. Rev. B* 61 (2000) 16117.
- [4] W.P. Meiklejohn, C.P. Bean, *Phys. Rev.* 102 (1956) 1413.
- [5] W.P. Meiklejohn, C.P. Bean, *Phys. Rev.* 105 (1957) 904.
- [6] J. Nogués, D. Lederman, T.J. Moran, I.K. Schuller, K.V. Rao, *Appl. Phys. Lett.* 68 (1996) 3186.
- [7] J. Nogués, T.J. Moran, D. Lederman, I.K. Schuller, K.V. Rao, *Phys. Rev. B* 59 (1999) 6984.
- [8] K. Liu, S.M. Baker, M. Tuominen, T.P. Russell, I.K. Schuller, *Phys. Rev. B* 63 (2001) 060403(R)
- [9] M. Kiwi, J. Mejía-López, R.D. Portugal, R. Ramírez, *Europhys. Lett.* 48 (1999) 573.
- [10] F. Nolting, A. Scholl, J. Stöhr, J.W. Seo, J. Fompeyrine, H. Siegart, J.-P. Locquet, S. Anders, J. Lüning, E.E. Fullerton, M.F. Toney, M.R. Scheinfeld, H.A. Padmore, *Nature* 405 (2000) 767.
- [11] M.v. Schilfgaarde, F. Herman, *Phys. Rev. Lett.* 71 (1993) 1923.
- [12] N.C. Koon, *Phys. Rev. Lett.* 78 (1997) 4865.
- [13] H. Ohldag, A. Scholl, F. Nolting, S. Anders, F.U. Hillebrecht, J. Stöhr, *Phys. Rev. Lett.* 86 (2001) 2878.
- [14] T. Oda, A. Pasquarello, R. Car, *Phys. Rev. Lett.* 80 (1998) 3622.
- [15] Ph. Kurz, G. Bihlmayer, K. Hirai, S. Blügel, *Phys. Rev. Lett.* 86 (2001) 1106.
- [16] C. Noguera, *J. Phys.: Condens. Matter* 12 (2000) R367.
- [17] P. Blaha, K. Schwarz, J. Luitz, WIEN97, Vienna University of Technology, 1997. (Improved and updated UNIX version of the original copyrighted WIEN code, published by P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, *Comput. Phys. Comm.* 59 (1990) 399.
- [18] I. de P.R. Moreira, R. Dovesi, C. Roetti, V.R. Saunders, R. Orlando, *Phys. Rev. B* 62 (2000) 7816.
- [19] Y. Zhou, D. Wang, Y. Kawazoe, *Phys. Rev. B* 59 (1999) 8387.
- [20] L.J. de Jongh, A.R. Miedema, *Adv. Phys.* 23 (1974) 1.
- [21] M.T. Hutchings, et al., *Phys. Rev. B* 2 (1970) 1362.
- [22] D. Lederman, Ph.D. Thesis, University of California, Santa Barbara, 1995, unpublished.
- [23] S. Frota Pessoa, R.B. Muniz, J. Kudrnovsky, *Phys. Rev. B* 62 (2000) 5293.