Mechanism of magnetization enhancement at CoO/permalloy interfaces

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The advertisement for the Lake Shore CRYOTRONICS Model PS-100 Preconfigured Tabletop Probe Station features a photograph of the device. The device is a complex mechanical assembly with various components, including a probe head, a sample stage, and a base. It is set against a blue background. The text 'NEW' is in orange, and 'Model PS-100' is in large, bold, dark blue. Below it, 'Preconfigured Tabletop Probe Station' is in a smaller, dark blue font. The Lake Shore CRYOTRONICS logo is on the right, with 'Lake Shore' in white and 'CRYOTRONICS' in dark blue. Below the logo, the tagline 'An affordable solution for a wide range of research' is written in a white, italicized font.

Mechanism of magnetization enhancement at CoO/permalloy interfaces

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We investigate the magnetic properties of CoO(111)/permalloy(111) interfaces by *ab-initio* calculations. We employ a $(5 \times 5)\text{CoO}/(6 \times 6)\text{permalloy}$ supercell, to satisfy the $\sim 5:6$ ratio of the lattice constants, and optimize the atomic density near the interface. While experimentally the interface magnetization is 14% higher than in the bulk, we find for the purely O/Co-terminated interface a decrease/increase by 140%/40%, which enables insight into the real interface with partial O deficiency and atomic intermixing. Intermixing between Fe and Ni significantly lowers the total energy, which promotes Fe accumulation at the interface. Since Co-O bonds are energetically favorable, O diffusion into the permalloy is suppressed. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818507>]

Materials exhibiting exchange bias¹ and perpendicular anisotropy are important for ultra-high density perpendicular recording media.² Among them, the CoO/Permalloy (Py) system is very attractive, since the Néel temperature of CoO is close to room temperature and the magnetocrystalline anisotropy is high. Although the physical properties of CoO/Py interfaces have been studied in various experimental works,^{3,4} an adequate characterization of the structural, electronic, and magnetic properties on an atomic level is missing. Insight can be obtained from first principles calculations based on density functional theory. However, it is important to notice that a major difficulty in studying interfaces between metals and metal oxides theoretically is the typically large lattice mismatch. Therefore, any calculation employing a coherent model (i.e., assuming that the lattice parameters of the component materials are the same) will give doubtful results, due to the induced strain.

The only way to avoid this problem is the construction of a large supercell that makes it possible to adjust the lattices of the two compounds.^{5–8} Also, one should take into account that even though the atomic distances in the bulk-like region of such a supercell should be close to the experimental bulk values the structure at the interface can be different. For example, in Ref. 6, first principles calculations have been employed to establish the variation of the Ni atomic density when approaching the CoO/Ni interface. In addition, the density has been found to change significantly with the type of interface termination. In this context, we study the magnetic properties of the CoO/Py interface due to its technological importance. We particularly explain why experiments find an enhancement of the magnetization at the interface, employing a first principles approach that takes into account the variation of the atomic density in the vicinity of the interface. The established mechanism is of general validity for many exchange bias systems.

To deal with the problem of 21% lattice mismatch between CoO and Py, we build a supercell that comprises 25 unit cells of CoO and 36 unit cells of Py per layer (in the

bulk-like regions) similar to the CoO/Ni interface in Ref. 5, see Fig. 1(a). This procedure reduces the lattice mismatch at the CoO/Py interface to less than 0.2%. Since the lattice parameters of Ni and Fe are similar, we can safely assume that the structure of the CoO/Py interface (here, $\text{Py} = \text{Ni}_{80}\text{Fe}_{20}$) is similar to that of CoO/Ni. For the latter, it has been found that O-termination enforces the atomic density in the first Ni layer to be the same as in the O layer next to it, see Fig. 1(b), because the Ni atoms prefer to resemble the structure of NiO. The second Ni layer turns out to be a transition layer in which atoms occupy hollow sites of the first Ni layer or of bulk-like Ni (3rd Ni layer). In the case of Co-termination, the first Ni layer is in contact with Co atoms, see Fig. 1(c). Since Co and Ni have similar lattice parameters, it is likely that the structure of this layer is similar to that of the 2nd Ni (Py) layer in the O-terminated CoO/Ni interface (first Ni layer in Fig. 1(c) and second Ni layer in Fig. 1(b)). Moreover, the 2nd Ni in the case of Co-termination resembles the structure of bulk Ni, see Fig. 1(c).

The transition layer comprises 31 Ni atoms located between layers of 5×5 and 6×6 atoms, at the O-terminated interface between 25 and 36 Ni atoms and at the Co-terminated interface between 25 Co and 36 Ni atoms. The importance of the transition layer can be understood from the hard sphere model shown in Fig. 2. If it would have the same structure as either the top or the bottom layer then there would be on-top sites, see Figs. 2(b) and 2(c), with nonphysical (too short) atomic distances. In Fig. 2(c), the transition layer has partially the structure of the bottom layer (area II) and partially the structure of the top layer (area I). In fact, there are many possible configurations of the transition layer where each atom occupies a hollow site of at least one adjacent layer. However, the most stable of these configurations is the one shown in Fig. 2(d). To approximate $\text{Py} = \text{Ni}_{80}\text{Fe}_{20}$, we substitute 5, 6, and 7 Ni atoms by Fe in the layers with 25, 31, and 36 atoms, respectively. 5 Py and 4 CoO layers are sufficient to have both the bulk-like regions and the CoO/Ni interface well represented in the supercell. The substitution of Ni by Fe is random and test calculations show that different configurations do not change the average value of the magnetization per layer.

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FIG. 1. (a) $(5 \times 5)\text{CoO}/(6 \times 6)\text{Ni}$ interface. The structure of the first two Ni layers (Ni1 and Ni2) depends on the termination of the interface: (b) O-terminated and (c) Co-terminated. In (b), the atoms of the first Ni layer occupy the hollow sites of the adjacent O layer. The second Ni layer is a transition layer. In (c), the atoms of the first Ni layer form the transition layer. Both CoO and Ni have (111) orientation.

For our first principles calculations, we use the Vienna *ab-initio* simulation package, which is based on the plane wave approach.^{9–11} For the exchange correlation potential, we use the generalized gradient approximation (GGA).¹³ In addition, we employ projector augmented wave pseudopotentials^{11,12} with the electronic configurations O $2s^2 2p^4$, Co $3d^8 4s^1$, and Ni $3d^9 4s^1$. We have verified that 15 Å of vacuum is sufficient to avoid artificial interaction across this region and that a plane wave basis set with energies up to 400 eV is accurate. A Γ -point calculation is sufficient because of the large size of our supercells ($14.96 \text{ Å} \times 34.44 \text{ Å}$). Moreover, the density of states (DOS) is calculated with a Gaussian smearing of 0.05 eV. To account for the localization of the $3d$ orbitals in CoO, we consider an onsite Coulomb interaction in the rotationally invariant Dudarev scheme (GGA + U)^{14–16} with an effective value of $U = 6.1 \text{ eV}$ for Co.^{17,18} The $3d$ orbitals of the Ni and Fe atoms at the O-terminated interface are subject to strong Coulomb repulsion if they bond to O (similar to NiO, FeO), whereas towards the bulk Py rather free carriers dominate. While the GGA works reasonably well for metals, it is known to underestimate the magnetic moments and band gaps in transitional metal oxides. The GGA + U approach can overcome this problem for metal oxides, but is not appropriate for metals. To compensate for this inaccuracy in our calculations, we employ both the GGA and GGA + U methods for the interface atoms and compare the results, whereas all other atoms in Py are treated without onsite interaction. The effective interaction parameter for the interface Ni and Fe atoms is taken from bulk NiO (5.0 eV for Ni) and FeO (3.6 eV for Fe), respectively.^{19,20}

In Ref. 3, it has been shown that the magnetization at the CoO/Py interface is 14% higher (800 emu/cm^3) than it is in bulk Py (700 emu/cm^3). In accordance with the theory of magnetic interaction, the presence of O at the CoO/Py interface should induce superexchange and thus antiferromagnetic coupling between the Co and Py atoms, if the Co-O-Py angle is close to 180° . Large deviations from 180° due to atomic disorder or O vacancies can lead to ferromagnetic coupling instead. This is the reason why a large lattice

FIG. 2. (a) The transition layer is located between a top layer of 25 and a bottom layer of 36 close packed atoms. (b)–(d) Possible structures of the transition layer. Yellow triangles (circles) indicate atoms occupying hollow (top) sites.

mismatch at a metal-oxide interface results in a complex magnetic behavior. Atomic disorder at the interface counteracts superexchange even when there is enough O available. For instance, in Ref. 4, it has been demonstrated that only 10% of the Co spins at the CoO/Py interface are antiferromagnetically coupled to the (ferromagnetic) Py and it has been argued that a significant amount of unpinned Co spins (follow an applied magnetic field) interacts ferromagnetically with the Py. These contributions is a result of the interface disorder.

The optimized structures of the O and Co-terminated CoO/Py interfaces are idealizations of a real interface with O vacancies and atomic intermixing. The reality thus lies somewhere in between the considered extremal cases. However, having understood the behavior of the ideal interfaces, we can extrapolate our knowledge to the real case. As mentioned before, a difficulty for first principles calculations arises for the interface atoms as they have bonds to metal atoms on one side and to O atoms on the other side (for example, Py at the O-terminated interface and Co at the Co-terminated

FIG. 3. Schematic picture of the magnetization directions at the (left) Co-terminated and (right) O-terminated CoO/Py interfaces.

interface). The onsite interaction parameter consequently cannot be defined unambiguously and our calculations have to be performed applying both methods (GGA and GGA + U) for the interface atoms. We evaluate the magnetic moment as the average value $M = (M^{GGA} + M^{GGA+U})/2 \pm \Delta M$, with a maximal error of $\Delta M = |M - M^{GGA+U}|$.

Separating the supercell in interface and bulk-like regions, as shown in Fig. 3, it has been demonstrated in Ref. 5 by GGA + U calculations that the bulk Ni magnetization of 558 emu/cm^3 decreases by 36% at the O-terminated interface, whereas at the Co-terminated interface, it doubles to 1073 emu/cm^3 , see Fig. 4. Here, we substitute 20% of the Ni by Fe for both interface terminations and find an increased magnetization 848 emu/cm^3 in the bulk-like Py region. This small discrepancy between theory and experiment (800 emu/cm^3) can be explained by the unavoidable domain structure in the real system, which lowers the overall magnetization with increasing temperature, while our first principles calculations assume zero temperature. As compared to the bulk-like Py region, the

FIG. 4. (a) Magnetization obtained for CoO/Py and CoO/Ni (Ref. 5), and experimental value (Ref. 3). Error comes from the interface atoms for which repulsion parameter is unknown.

magnetization of Py at the O-terminated interface significantly increases to $1211 \pm 142 \text{ emu/cm}^3$, due to the oxidation of the Fe/Ni atoms. Taking into account the magnetization of the uncompensated interface Co atoms ($-2636 \pm 38 \text{ emu/cm}^3$), we obtain a total magnetization at the interface of $320 \pm 66 \text{ emu/cm}^3$, which is 62% smaller than in the bulk-like Py region. As we can see from Fig. 4, the O-terminated interface shows an antiferromagnetic coupling between the Co and Py atoms. The interface magnetization is oriented opposite to that in the bulk-like Py region, since the magnetic moments of the Co atoms directly at the interface are larger (with opposite sign) than those of the Py atoms. At the Co-terminated interface, the Co atoms are less oxidized ($1755 \pm 171 \text{ emu/cm}^3$) as compared to the O-terminated interface, since O atoms are located only on one side. The magnetization of the interface Py layer is 726 emu/cm^3 , which is slightly smaller than in the bulk-like region, since the Py atomic density decreases towards the interface. The magnetization of the Co-terminated interface is $1189 \pm 31 \text{ emu/cm}^3$ and thus, 40% higher than in the bulk-like Py region. Of course, the magnetization of bulk CoO is zero as it is an antiferromagnet. If we use for the orbital moments of Co, Ni, and Fe, the values of their oxides ($1.24 \mu_B$ for Co,²¹ $0.29 \mu_B$ for Ni,²² and $0.88 \mu_B$ for Fe, Ref. 23) the magnetization of the O-terminated interface decreases to $165 \pm 64 \text{ emu/cm}^3$ and that of the Co-terminated interface increases to $1607 \pm 21 \text{ emu/cm}^3$. However, the conclusions stay the same.

While the calculated magnetization of bulk Py is comparable to the experimental value, the magnetizations obtained for the two interfaces (O-terminated and Co-terminated) are very different. This fact implies that a realistic interface is neither O nor Co-terminated but rather a mixture of these two extreme cases. For instance, the O vacancies in a real CoO/Py interface lead to both Py-Co and Py-O-Co bonding at the same time, where Py atoms in contact with Co and O will show opposite moments. Co atoms in contact with Py have a slightly smaller magnetic moment ($2.66 \mu_B$) than those in contact with O ($2.76 \mu_B$) but with the same orientation as the moments of the Py atoms. Hence, the magnetization is expected to grow with the number of O vacancies. Another reason for the observed discrepancy between experiment and our model is the intermixing between the interface

FIG. 5. Changes of the CoO/Py interface energy by intermixing.

atoms. Our calculations show that such an intermixing of the interface Fe and Co atoms lowers the total energy of the system by 0.14 eV/atom, while an intermixing of the interface Ni and Co atoms increases the energy by 0.33 eV/atom, see Fig. 5. Interestingly, we obtain a large reduction of the total energy (0.73 eV/atom) when there is an intermixing between the Fe atoms of the bulk-like Py region and the interface Ni atoms. Thus, there is an incentive to increase the Fe concentration at the CoO/Py interface. This observation can be explained in terms of the electronegativity, which is lowest for Fe (1.83 eV), medium for Co (1.88 eV), and highest for Ni (1.91 eV). As a consequence, the bonds between the Fe and O atoms are stronger than those between the O and Ni or Co atoms. We can conclude that at the CoO/Py interface processes are energetically favorable that create additional Fe-O bonds: (1) Fe-Co intermixing and (2) intermixing of the interface Ni and bulk-like Fe atoms. Also, since bulk Co has a higher oxidation energy than bulk Ni and the amount of Fe atoms in Py is small as compared to Ni, diffusion of O atoms from CoO into the bulk-like Py region is less probable.

In conclusion, a supercell containing different numbers of CoO and Py unit cells (in order to reduce the lattice mismatch) and a transition layer of intermediate atomic density is able to correctly describe the bulk-like regions of the CoO/Py interface. However, when one approaches the interface, the experimental and calculated values of the magnetization deviate considerably. For instance, while the experiment finds for the bulk-like Py region a magnetization of 700 emu/cm³, this value increases to 800 emu/cm³ at the interface with CoO where 90% of the Co atoms are coupled ferromagnetically to Py atoms. Our results demonstrate that the magnetization of the bulk-like Py region (848 emu/cm³) decreases to 320 ± 66 emu/cm³ at the O-terminated interface due to anti-ferromagnetic coupling and increases to 1189 ± 31 emu/cm³ at the Co-terminated interface due to ferromagnetic coupling. This discrepancy proves the presence of O vacancies and/or interface intermixing, as to be expected for finite temperature. The magnetization values of the O and Co-terminated interfaces clearly show that more O vacancies enhance the interface

magnetization. At the same time, our result point to a vanishing probability of O diffusion into the bulk-like Py region and a strong tendency of the Fe atoms accumulate at the interface. Understanding of the thermal processes leading to the interface disorder would be welcome and could be realized by molecular dynamics simulations. However, this approach requires an enormous amount of computational resources due to the large lattice mismatch that needs to be taken into account to obtain valid results.

- ¹W. Meiklejohn and C. Bean, *Phys. Rev.* **102**, 1413 (1956).
- ²J. Nogues and I. Schuller, *J. Magn. Magn. Mater.* **192**, 203 (1999).
- ³S. Roy, C. Sanchez-Hanke, S. Park, M. R. Fitzsimmons, Y. J. Tang, J. I. Hong, D. J. Smith, B. J. Taylor, X. Liu, M. B. Maple, A. E. Berkowitz, C. C. Kao, and S. K. Sinha, *Phys. Rev. B* **75**, 014442 (2007).
- ⁴E. Blackburn, C. Sanchez-Hanke, S. Roy, D. J. Smith, J. I. Hong, K. T. Chan, A. E. Berkowitz, and S. K. Sinha, *Phys. Rev. B* **78**, 180408(R) (2008).
- ⁵S. Grytsyuk, F. Cossu, and U. Schwingenschlögl, *Eur. Phys. J. B* **85**, 254 (2012).
- ⁶S. Grytsyuk, M. V. Peskov, and U. Schwingenschlögl, *Phys. Rev. B* **86**, 174115 (2012).
- ⁷R. Benedek, A. Alavi, D. N. Seidman, L. H. Yang, D. A. Muller, and C. Woodward, *Phys. Rev. Lett.* **84**, 3362 (2000).
- ⁸R. Benedek, D. N. Seidman, M. Minkoff, L. H. Yang, and A. Alavi, *Phys. Rev. B* **60**, 16094 (1999).
- ⁹G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- ¹⁰G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹¹G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹²P. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ¹³J. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ¹⁴V. Anisimov, J. Zaanen, and O. Andersen, *Phys. Rev. B* **44**, 943 (1991).
- ¹⁵V. Anisimov, I. Solovyev, M. Korotin, M. Czyzyk, and G. Sawatzky, *Phys. Rev. B* **48**, 16929 (1993).
- ¹⁶S. Dudarev, G. Botton, S. Savrasov, C. Humphreys, and A. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- ¹⁷T. Bredow and A. Gerson, *Phys. Rev. B* **61**, 5194 (2000).
- ¹⁸F. Tran, P. Blaha, K. Schwarz, and P. Novak, *Phys. Rev. B* **74**, 155108 (2006).
- ¹⁹O. Bengone, M. Alouani, P. Blöchl, and J. Hugel, *Phys. Rev. B* **62**, 16392 (2000).
- ²⁰N. J. Mosey, P. Liao, and E. A. Carter, *J. Chem. Phys.* **129**, 014103 (2008).
- ²¹U. D. Wdowik and K. Parlinski, *Phys. Rev. B* **78**, 224114 (2008).
- ²²S. K. Kwon and B. I. Min, *Phys. Rev. B* **62**, 73 (2000).
- ²³S. A. Gramsch, R. E. Cohen, and S. Y. Savrasov, *Am. Mineral.* **88**, 257 (2003).