**Spontaneous exchange bias formation driven by a structural phase transition in the antiferromagnetic material**

A. Migliorini1, B. Kuerbanjiang2, T. Huminiuc2, D. Kepaptsoglou3, M. Muñoz4, J. L. F. Cuñado5,6, J. Camarero5,6,7, C. Aroca1, G. Vallejo-Fernández2, V. K. Lazarov2, J. L. Prieto1\*

1 Instituto de Sistemas Optoelectrónicos y Microtecnología-ISOM. Universidad Politécnica de Madrid. Avda. Complutense 30, 28040, Madrid, Spain.

2 Department of Physics, University of York, York YO10 5DD, United Kingdom.

3 SuperSTEM, STFC Daresbury Laboratories, Keckwick Lane, Warrington, WA4 4AD, United Kingdom.

4 IMN-Instituto de Micro y Nanotecnología, (CNM-CSIC), Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain.

5 IMDEA-Nanoscience, c/ Faraday, 9 Campus de Cantoblanco, 28049 Madrid, Spain.

6 DFMC and Instituto “Nicolás Cabrera”, Universidad Autónoma de Madrid, 28049 Madrid, Spain.

7 Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain.

**Exchange Bias** **is a very useful magnetic interaction that couples a ferromagnetic and an antiferromagnetic material, resulting in a unidirectional displacement of the ferromagnetic hysteresis loop by an amount called the ‘exchange bias field’. Setting and optimizing Exchange Bias involves cooling through the Néel temperature of the antiferromagnetic material in presence of a magnetic field. Here we demonstrate an alternative process for the generation of Exchange Bias. In IrMn/FeCo bilayers, a structural phase transition in the IrMn layer develops at room temperature, exchange biasing the FeCo layer as it propagates. Once the process is completed, the IrMn layer contains very large single crystal grains, with a large density of structural defects within each grain, which are promoted by the FeCo layer. The magnetic characterization indicates that these structural defects in the antiferromagnetic layer are behind the resulting large value of the exchange bias field and its good thermal stability.** **This mechanism to establish the Exchange Bias can help clarifying fundamental aspects of this exchange interaction.**

Exchange Bias (EB)1,2 is a fundamental magnetic interaction behind many experiments in modern magnetism3. This interfacial coupling is also at the core of an immense variety of magnetic devices and sensors4, including hard drive reading heads5, Magnetic RAMs or Spin Transfer Torque MRAMs6. Not surprisingly, the research devoted to this effect in the last two decades has been, and still is, very intense, making this interface interaction one of the most relevant in modern science.

A variety of systems such as nanoparticles, epitaxial bilayers or polycrystalline thin films, can show EB. In all of them, the EB is achieved by thermal activation of the spins at the boundary between the antiferromagnetic (AF) and the ferromagnetic (F) material. This thermal setting involves cooling (or growing) the bilayer in a static magnetic field, below the Néel temperature of the AF, resulting in a unidirectional exchange anisotropy at the F/AF interface. The macroscopic signature of this interfacial exchange interaction is a shift in the hysteresis loop along the field axis. In most systems, the loop shifts in the opposite direction to the setting external magnetic field (‘negative’ EB), although a ‘positive’ shift in the same direction of the setting field has also been observed7 (‘positive’ EB).

Among all the possible AF materials, IrMn is widely used in magnetoresistive sensor technology due to its high Néel temperature, large anisotropy and resistance to corrosion8. The EB setting process in polycrystalline IrMn is done via thermal activation of the AF grains9,10 and the value of the EB field is enhanced by a strong (111) grain texture parallel to the F/AF interface11. The AF grains switch their magnetic orientation independently following a Néel-Arrhenius law, as they are not exchange coupled to each other12. The energy barrier for the switching can be low enough to allow room temperature EB setting13,14 or it can be reduced by the interfacial exchange with the F layer15,16 but again, the EB setting can only be achieved via thermal activation of the separate grains. Consequently, the setting process affects the entire sample and a microscopic control of the EB direction is not possible unless the sample is locally treated with laser or ion radiation17,18.

In this article, we describe a physical process for the generation of EB. We have fabricated IrMn/FeCo bilayers where the EB forms spontaneously at Room Temperature (RT), nucleating at scattered points across the sample and then propagating following a structural phase transition in the IrMn layer. The direction of the EB can be selected arbitrarily by simply changing the orientation of the magnetization in the FeCo layer as the phase transition propagates. This process, which allows microscopic control of the Exchange Bias, opens the door to explore local magnetic interactions at the interface19,20,21 and to design innovative devices.

**Spontaneous Exchange Bias formation**. The samples were deposited by magnetron sputtering as described in Methods. Immediately after deposition, the samples are measured in a Vibrating Sample Magnetometer and they show a hysteresis loop like the one with open black circles in figure 1a. This hysteresis loop shows no EB or coercivity enhancement and it is virtually the same as the one associated with a single FeCo layer of the same thickness. Just by leaving the sample at RT, with the FeCo layer in its remanent state (positive field in figure 1a), the EB develops spontaneously over the next couple of days (hysteresis loop with blue dots in figure 1a). The exchange bias field, *Heb*, is of the order of 600 Oe in this sample but it can reach 750 Oe in other samples (*Jex*=0.65 erg/cm2). Once formed, the EB survives repeated cycling of an external magnetic field of ±1.4 T (figure S1 in Supplementary Information). In between the two measurements presented in figure 1a, the sample is taken to the X-Ray Diffractometer (XRD) for structural characterization. Figure 1b shows periodic *θ*-2*θ* scans measured every 1.5 hours around the position of the IrMn (111) reflection. The IrMn (111) diffraction peak, initially absent, raises rapidly and its area increases with time following a sigmoidal function, as shown in figure 1c. The increasing intensity of the peak could indicate either a spontaneous crystallization in the IrMn layer with enhanced (111) texture or a reorientation of the IrMn grains, such as an increase in the texture or a decrease of the mosaicity. Rocking curve measurements, taken at different stages of the spontaneous EB formation (figure S3 of Supplementary Information), indicate that there is no reorientation of the IrMn grains.

A sample deposited in the same run to the one measured in figures 1a, b and c, was used to perform magnetic characterization. Figure 1d shows how the EB develops in the sample after deposition, just by leaving it at RT in the remanent state of the FeCo. Remarkably, there is an increase in both the proportion of the hysteresis loop showing EB and the value of the EB field itself. This suggests that an increasing area of the FeCo is getting exchanged biased with time. We can confirm this point by taking Kerr images of the sample at particular times during this spontaneous EB setting. Figure 1e shows a Kerr image of the surface of the FeCo layer 8 hours after deposition, which corresponds to the hysteresis loop with red filled circles in figure 1d. By cycling the external field between different positive and negative values, we can conclude that the areas with dark contrast are free and the areas with light contrast are exchange biased to the IrMn (see Movie 1 in Supplementary Material). A Kerr image of the sample 14 hours after deposition is shown in figure 1f, and it confirms that the areas with exchange biased FeCo (light contrast) have grown and merged together, leaving only a few zones where the FeCo is still free (dark contrast).

Figure 1g represents the evolution with time of the proportion of the hysteresis loop that shows exchange bias (*Meb*), normalized to the total magnetization of the loop (*Mtot*). Effectively, *Meb/Mtot* represents the area of the growing domains in the IrMn that are exchange biasing the FeCo as they grow, normalized to the total area of the sample. The sigmoidal shape of the curve showing the development of the EB in figure 1g is almost identical to the curve describing the structural development in figure 1c. This indicates that the structural change described in figures 1b and 1c is the cause of the progressive development of the EB that is shown in figures 1d and 1g. This sigmoidal shape is typical of a two-dimensional growth and it fits well to the Avrami model22, originally used to describe phase transformations in solids at constant temperature (see Supplementary Information). Therefore, the IrMn seems to undergo a spontaneous structural phase transformation at room temperature, which drives the formation of the EB in the FeCo layer. This structural phase transformation could either be a crystallization from an initially amorphous or nanocrystalline state or another type of phase transition. For instance, we could be observing a transition from a disordered γ-IrMn3 to ordered L12-IrMn3 (figures 2a and 2b), which could also have a significant impact on both the EB and the shape of the hysteresis loop23. In order find out what type of phase transition takes place in the IrMn layer, we performed a detailed structural characterization on different samples.

**TEM characterization of the samples.** We analyzed samples with and without the ferromagnetic FeCo layer on top of the IrMn, in order to evaluate the role of the FeCo in the phase transformation of the IrMn. Figure 2 shows paired images (plan-view TEM and Selective Area Diffraction – SAD) of a sample without FeCo, taken at different times during the phase transition of the IrMn. Soon after deposition, the IrMn is nanocrystalline (figures 2c and 2e). After a few hours, large crystals of IrMn grow spontaneously from different nucleation points across the sample. These IrMn single crystal grains are oriented in the (111) direction as shown by SAD in figure 2f, which agrees with the XRD measurement shown in figure 1b. The phase transition can be observed live in Movie 2 of Supplementary Material. The atomic structure of IrMn, once fully crystalline, is that of a disordered γ-IrMn3 phase. To the best of our capabilities, we have not detected the presence of the ordered L12-IrMn3 phase (see also figures S4 to S8 in Supplementary Information). The final crystalline phase of the IrMn contains very large single crystal grains of a typical lateral size in the range of 100 nm (see figure S8).

The IrMn layer undergoes the crystallization process independently of the type of substrate (Si, Si/SiO2 or TEM grid) and on what is deposited on top of the IrMn layer. Neither the ordering structure (i.e. γ- versus L12-IrMn3) nor the grain size of the IrMn depend on the presence of the FeCo layer. However, the ferromagnetic FeCo layer plays a crucial role in the formation of structural defects in the IrMn layer. Figure 3 shows illustrative images comparing the crystalline IrMn in samples without (figure 3a) and with (figure 3b) FeCo on top of the IrMn. The samples with FeCo deposited on top of the IrMn layer show a much larger number of defects within each IrMn crystalline grain. Figure 3c and 3d show high-resolution images of two of the frequent antiphase boundaries (APB) and stacking fault boundaries found in the IrMn layer when it crystallizes with the FeCo layer on top. The IrMn in the sample without FeCo can host defects such as twin defects and stacking faults, with much lower density. We note that APBs are only (and frequently) present in the sample with FeCo on top of the IrMn. An important number of these structural defects induced by the FeCo layer seem to have their origin in the polycrystalline nature of the FeCo, although the magnetic exchange interaction at the interface may also be playing a role and this option could not be ruled out. The structural defects in the IrMn seem to play a pivotal role in the formation and in the thermal stability of the EB as we discuss in the next section.

**Magnetic characterization after crystallization of the IrMn layer**. Once the spontaneous crystallization of the IrMn is finished, the FeCo layer is exchange biased to the IrMn as shown in figure 1. In order to test the thermal stability of the EB we performed several experiments. We started with a reversal experiment at room temperature (RT). The direction of the magnetization in the FeCo layer is reversed 180º with respect to its original EB direction, by leaving the sample in a magnetic field large enough to saturate the biased FeCo layer. The sample was permanently under the saturating magnetic field except when the hysteresis loop was measured. Figure 4a and 4b show that the EB relaxation at RT is very slow. The data, plotted against a ln(*t*) scale (figure 4b, inset), deviate from a linear behavior. This is likely the result of having a distribution of activation energies, *KAF·V*, being *KAF* the anisotropy of the IrMn and *V* the volume of the IrMn involved in the EB24. The data from figure 4b can also be fitted to the single formula derived by Xi *et al*.25 to describe exchange bias field (*Heb*) relaxation in reverse magnetic fields,

(1)

The experimental points of figure 4b fit to equation (1) resulting in the following values: *β*=0.47 and *τ*=11,225 h (solid line in Fig. 4b). The standard error in the fitting is 1.6% for *β* and 6% for*τ*, which shows that the very large value of *τ* obtained from a measurement that takes just over 800 h can be trusted.

For a *β*<1, the behavior with temperature of the characteristic time *τ* follows the Arrhenius law9,25

(2)

where *kB* is the Boltzmann constant, *T* the temperature and *υ0* the characteristic attempt frequency whose value for IrMn was measured as 2.1·1012 Hz (see Methods). Therefore, for *τ*=11,225 h and *T*=300 K, an energy barrier of *Eb*= *KAF·V* =1.6·10-12 erg is obtained. Taking the anisotropy of IrMn as 8·106 erg/cm3, which also fits some results shown later, would lead to a median volume of IrMn involved in the EB of *V*=240 nm3. This grain volume is clearly smaller than the real grain size revealed by TEM in the crystalline IrMn, which is in the range of several thousands of nm3. This is our first indication that each crystalline grain of IrMn is broken into antiferromagnetic domains. At first glance, having several magnetic domains within each large IrMn grain sounds quite plausible, particularly in the samples with FeCo where, as shown in figure 3b, the IrMn is packed with structural defects that can pin AF domain walls. Note also, that if the value of *KAF* was assumed to be smaller, for instance 5·105 erg/cm3, which is one of the lowest reported for IrMn, the lateral size of the IrMn volume involved in the EB would be ~14 nm, which is still considerably smaller than the crystalline size of the IrMn grains.

In order to provide further evidence of this possible multidomain configuration within each IrMn grain, we performed, on a different sample, a field annealing following the sequence described in Methods. The results are shown in figure 4c. Firstly, we can observe that the EB field, *Heb*, remains constant initially but it decreases sharply for setting temperatures higher than 410 K. This is a counterintuitive result as the thermal annealing should optimize the value of *Heb* in samples with polycrystalline IrMn. The sample does not seem to be suffering any deterioration during the setting at high temperatures as the inset to figure 4c shows. There is no loss in the magnetic moment of the sample and the shape of the hysteresis loop only gets squarer during the annealing. Additionally, the sample was checked by XRD after the annealing and no structural change was observed. Therefore, it seems that the decrease of *Heb* above 410 K may be caused by the thermal activation of the AF domain walls within each IrMn crystalline grain. In fact, when large AF grains are broken into magnetic domains, the EB field can either increase or decrease, depending on the amount and strength of the pinning sites for the antiferromagnetic domain walls26,27.

We can also infer the presence of the magnetic domains within each IrMn grain by fitting the curve of blocking temperature to the strong domain wall pinning model developed in Ref. 27 to interpret the effects of dopants and defects in exchange biased systems. The measurement of the blocking temperature <*TB*> and the fitting of the experimental data to the AF domain wall (AF-DW) pinning model (see Methods) are displayed in figure 4d. Although there is undeniably some uncertainty in some of the parameters used for the simulation, the good quality of the fitting shown in figure 4d gives confidence that our interpretation of the results is correct. Each large crystalline IrMn grain is broken into AF domains, with the AF-DWs strongly pinned, possibly at the frequent structural defects visible in figure 3b. As the activation temperature increases, some of these strongly pinned AF-DWs become unpinned, giving rise to a larger domain that no longer follows the Stoner-Wohlfarth model during reversal. This domain would therefore result in a lower contribution to the loop shift. This interpretation explains both the initial loss of *Heb* visible in figure 4c above 410 K (temperature at which strongly pinned AF-DW may start moving) and the fact that the red curve in figure 4d (blocking temperature), at high temperatures, tends towards a value of *Heb* which is smaller than the corresponding *Heb* at low temperatures (-500 Oe).

**Exchange Bias setting**. In order to provide an explanation of how the EB is established as the crystalline phase of the IrMn spreads across the sample, we can firstly go back to figure 4c. In this figure, we can notice that the coercive field decreases very quickly with increasing temperature, even for mild temperatures just above RT. The coercivity decrease is mainly due to the ascending branch of the hysteresis loop moving towards higher negative fields (see details in figure S9). This indicates that the field annealing is aligning rotatable magnetic moments at the IrMn/FeCo interface. These rotatable moments contribute to the coercivity enhancement of exchanged biased films28,29,30 and, after the crystallization of the IrMn layer, a percentage of them settles slightly misaligned with the EB direction, contributing to a large coercivity. As the temperature increases in the field annealing routine, these rotatable moments align better with the EB direction, decreasing the coercivity.

Another fact that should not go unnoticed is that, once the crystallization is finished, the EB field keeps increasing for a few days until it settles in its final value. This is visible in figure 1d (compare *Heb* in the cycle for 312 h with the trend that *Heb* follows during crystallization) and confirmed by the higher contrast of the areas that crystallized first, in any of the Kerr movies provided in Supplementary Material. This increase of the EB field soon after crystallization is quite relevant (20% to 25% increase) and it can reflect different scenarios. The first option would be that the crystalline structure of the IrMn may be evolving with time after the crystallization is completed. For instance, some areas may be changing spontaneously from disordered γ-IrMn3 phase to an ordered L12-IrMn3 phase. To the best of our capabilities, we have not detected the presence of the L12-IrMn3 phase at any time after crystallization, which leads us to propose an alternative origin for the EB.

We assume that, as the crystalline phase propagates, some magnetic moments at the IrMn/FeCo interface may settle strongly pinned, causing the initial loop shift. Then, the areas adjacent to these strongly pinned moments get exchange biased in the hours after the crystallization of the IrMn, likely driven by a direct exchange interaction. We can only speculate about the location of these pinned magnetic moments, but we note that strong uncompensated moments have been observed in phase domain walls, where the AF spin structure shifts laterally by one structural lattice constant31. Therefore, it seems plausible that defects within each grain in our IrMn (where the lattice constant is shifted) host strong uncompensated moments. Also, Ohldag *et al*.28 located the pinned uncompensated spins at the boundaries between crystallographic grains and established that about 4% of the interface in their samples contained pinned spins. Our TEM characterization and the AF-DW model used to fit the results of figure 4d, point towards ~1% density of structural defects, which is a similar value to the one found by Ohldag *et al*. in their samples28. Nevertheless, further characterization is required to test the validity of the proposed mechanism. For instance, it would be useful to reveal the precise configuration of the magnetic moments in the atoms around the structural defects in the IrMn layer, using for instance spin polarized scanning tunnel microscopy31. Also, samples with a thicker IrMn layer may provide stronger signals for a structural characterization that could clarify the precise role of the FeCo in the formation of the structural defects in the IrMn.

Finally, a particularly interesting feature of the spontaneous crystallization of the IrMn layer described in this work is that it allows the microscopic control of the EB direction. As the crystalline phase spreads across the sample, the direction of the magnetization in the FeCo layer can be changed and with it, the EB direction. Figure 5 shows a false colored Kerr photograph of a sample where the direction of the remanent magnetization of the FeCo layer has been switched 180º twice during the growth of the crystalline phase (see detailed sequence in Figure S10 of Supplementary Information). As the crystalline areas grow, they exchange bias the FeCo layer in the direction of its remanent magnetization. Figure 5 shows annular regions with EB in opposite directions (blue and green) and regions still unaffected by the crystallization (with no EB) in yellow (see also the magnetization process in Movie 3 of Supplementary Material).

We have described a physical process for the generation of EB, based on a room temperature spontaneous crystallization of the antiferromagnetic material. The EB is established by an alternative mechanism to the standard thermal annealing, which opens a window to studies on the interrelations between the value of the EB field and the configuration of the interfacial magnetic moments. The possibility of controlling the direction of the EB microscopically and the large average grain size of the crystallized IrMn, which is behind the good thermal stability of the EB, are also interesting features for devices based on these structures or for further research on the microscopic behavior of the Exchange Bias.

**References**

1 Nogués, J. & Schuller, I. K. Exchange Bias. *J. Magn. Magn. Mater*. **192,** 203 (1999).

2 Meiklejohn, W. H. & Bean, C. P. New Magnetic Anisotropy. *Phys. Rev.* **102,** 1413 (1956).

3 Jungwirth, T., Marti, X., Wadley, P. & Wunderlich, J. Antiferromagnetic spintronics. *Nature Nanotech*. **11,** 231 (2016).

4 Nogués, J. *et al*. Exchange bias in nanostructures. *Phys. Rep*. **442,** 65 (2005).

5 Dieny, B. *et al*. Giant magnetoresistive in soft ferromagnetic multilayers. *Phys. Rev. B* **43,** 1297 (1991).

6 Kent, A. D. & Worledge, D. C. A new spin on magnetic memories. *Nature Nanotech*. **10,** 187 (2015).

7 Nogués, J., Leighton, C. & Schuller, I. K. Correlation between antiferromagnetic interface coupling and positive exchange bias*. Phys. Rev. B* **61,** 1315 (2000).

8 Samant, M. G., Lüning, J., Stöhr, J. & Parkin, S. S. P. Thermal stability of IrMn and MnFe exchange-biased magnetic tunnel junctions. *Appl. Phys. Lett*. **76,** 3097 (2000).

9 van der Heijden, P. A. A. *et al*. Thermally assisted reversal of exchange biasing in NiO and FeMn based systems. *Appl. Phys. Lett.* **72,** 492 (1998).

10 Vallejo-Fernandez, G., Aley, N. P., Fernandez-Outon, L. E. & O’Grady, K. Control of the setting process in CoFe/IrMn exchange bias systems. *J. Appl. Phys.* **104,** 033906 (2008).

11 Imakita, K., Tusnoda, M., & Takahashi, M. Giant exchange anisotropy observed in Mn–Ir/Co–Fe bilayers containing ordered Mn3Ir phase. *Appl. Phys. Lett*. **85,** 3812 (2004).

12 O’Grady, K., Fernandez-Outon, L. E. & Vallejo-Fernandez, G. A new paradigm for exchange bias in polycrystalline thin films. *J. Magn. Magn. Mater*. **322,** 883 (2010).

13 Thomas, L. & Negulescu, B. Metastable antiferromagnetic domain configurations in exchange biased bilayers. *J. Appl. Phys.* **93,** 8606 (2003).

14 Paetzold, A. & Röll, K. Thermally activated self-alignment of exchange coupling in NiO/NiFe bilayers. *J. Appl. Phys.* **91,** 7748 (2002).

15 Craig, B. *et al*. A model of the temperature dependence of exchange bias in coupled ferromagnetic/antiferromagnetic bilayers. *J. Appl. Phys*. **103,** 07C102 (2008).

16 Vallejo-Fernandez, G., Kaeswurm, B., Fernandez-Outon, L. E., & O’Grady, K. Effect of the Ferromagnetic Layer Thickness on the Blocking Temperature in IrMn/CoFe Exchange Couples. *IEEE Trans. Magn*. **44,** 2835 (2008).

17 Mougin, A. *et al*. Local manipulation and reversal of the exchange bias field by ion irradiation in FeNi/FeMn double layers. *Phys. Rev. B* **63,** 060409(R) (2001).

18 Ueltzhöffer, T. *et al*. Néel walls between tailored parallel-stripe domains in IrMn/CoFe exchange bias layers. *J. Appl. Phys*. **117,** 123904 (2015).

19 Martí, X. *et al*. Electrical measurement of antiferromagnetic moments in exchange-coupled IrMn/NiFe stacks. *Phys. Rev. Lett.* **108,** 017201 (2012).

20 Wan, Y. Y. *et al*. Room-temperature perpendicular exchange coupling and tunneling anisotropic magnetoresistance in an antiferromagnet-based tunnel junction. *Phys. Rev. Lett.* **109,** 137201 (2012).

21 Morales, R. *et al*. Exchange-bias phenomenon: the role of the ferromagnetic spin structure. *Phys. Rev. Lett.* **114,** 097202 (2015).

22 Avrami, M. Kinetics of phase change. II transformation‐time relations for random distribution of nuclei. *J. Chem. Phys*. **8,** 212 (1940).

23 Kohn, A. *et al*. The antiferromagnetic structures of IrMn3 and their influence on exchange-bias. *Sci. Rep.* **3,** 2412 (2013).

24 El-Hilo, M., O’Grady, K., Chantrell, R. V. The origin of non-linear ln(t) behaviour in the time dependence of magnetisation. *J. Magn. Magn. Mater*. **109,** L164 (1992).

25 Xi, H., Franzen, S., Mao, S. & White, R. M. Exchange bias relaxation in reverse magnetic fields. *Phys. Rev. B* **75,** 014434 (2007).

26 Fecioru-Morariu, M., Ali, S. R., Papusoi, C., Sperlich, M. & Güntherodt, G. Effects of Cu dilution in IrMn on the exchange bias of CoFe/IrMn bilayers. *Phys. Rev. Lett.* **99,** 097206-1 (2007).

27 Vallejo-Fernandez, G., Kaeswurm, B. & O’Grady, K. Defect and impurity effects in exchange bias systems. *J. Appl. Phys.* **109,** 07D738 (2011).

28 Ohldag, H. *et al.* Correlation between Exchange Bias and Pinned Interfacial Spins. *Phys. Rev. Lett.* **91,** 017203 (2003).

39 Zhou, X. *et al*. Mapping motion of antiferromagnetic interfacial uncompensated magnetic moment in exchange-biased bilayers. *Sci. Rep.* **5,** 9183 (2015).

30 Wu, J. *et al.* Direct Measurement of Rotatable and Frozen CoO Spins in Exchange Bias System of CoO/Fe/Ag(001). *Phys. Rev. Lett.* **104,** 217204 (2010).

31 Bode, M., *et al*. Atomic spin structure of antiferromagnetic domain walls. *Nature Mater*. **5,** 477 (2006).

32 Vallejo-Fernandez, G., Aley, N. P., Chapman, J. N. & O’Grady, K. Measurement of the attempt frequency in antiferromagnets. *Appl. Phys. Lett.* **97**, 222505 (2010).

**Methods**

The samples were deposited by magnetron sputtering on 10×5 mm2 Si/SiO2 and Si(100) substrates at RT, under a 300 Oe magnetic field and with an Ar pressure of 6 mTorr. The structure of the samples is Substrate/Ta(3.5)/IrMn(15)/Fe40Co60(5), with the numbers in brackets indicating the thickness in nanometers. The structure is capped either with Cu(7)/Pt(1.5) or with Ta(5), depending on the measurement to be performed on the sample. All the layers were deposited at a high deposition rate: 0.58, 0.50, 0.56, 0.40 and 0.58 nm/s for the Ta, IrMn, FeCo, Cu and Pt layers, respectively. The IrMn layer is deposited by RF sputtering from a target of nominal composition IrMn3. The composition, measured in different samples by Energy-dispersive X-ray spectroscopy in a Transmission Electron Microscope (TEM), is on average Ir30Mn70, although in the text we generally refer to this layer simply as IrMn.

Cross-sectional transmission electron microscopy (TEM) samples were prepared by conventional methods including mechanical thinning and Ar ion milling. Plan-view TEM samples were prepared by depositing the films on carbon support film TEM grids. Selected area electron diffraction (SAD) was recorded using TEM (JEOL 2011), while atomic level structural study was performed by aberration-corrected JEOL 2200FS and Nion UltraSTEM 100 microscopes operating at 200 kV and 100 kV, respectively.

The thermal setting of the EB (sometimes referred as the York protocol; see details in ref. 12) consists in the following steps: the temperature of the sample is raised to a given setting temperature *Tset* in the presence of 1 T magnetic field. The sample stays at that temperature and in 1 T field for 90 min. Then the sample is cooled down to a temperature, *Tna*, where there is no thermal activation in the grains of the IrMn. For our samples Tna=300 K. A first hysteresis loop is cycled to remove the training effect and then the hysteresis loop is measured.

Following the York setting routine, the blocking temperature is found by repeating the following sequence: the EB is set to its maximum in one direction (negative in figure 4d), the temperature is then raised to a given activation temperature (*Tact*) in the presence of a -1 T and this situation is maintained for 30 min. Then the temperature is decreased to 300 K, a first hysteresis loop is cycled to remove the training effect and then a measurement is taken. The routine is repeated for increasing values of *Tact*. The temperature at which *Heb* goes to zero is known as the blocking temperature. At this temperature half of the sample is exchanged biased in one direction and the other half in the opposite.

For the antiferromagnetic domain wall pinning model used to fit the experimental results of figure 4c, we assumed that each large crystallographic defect (APB or Twin defect) may host an AF domain wall (AF-DW), breaking the large IrMn grain into smaller magnetic volumes. If some of these volumes are large enough (typically 20nm lateral size), they may accommodate more AF-DWs also subject to pinning sites. If the volume is small, it would behave as a quasi-single domain so it switches by rotation over an energy barrier *KAF·V*. The defects pinning the AF-DWs have different energies. Defects with an energy greater than 30 *kB·T* could be strong enough to pin an AF domain wall. The value 30 *kB·T* is chosen to be stronger than the 25 *kB·T* critical energy barrier, which corresponds to a measurement time of 100 s, but not so strong that moderate temperatures fail to unpin the domain wall from the defect. Defects with energy lower than 30 *kB·T* would not be strong enough to pin an AF-DW and hence have no effect on the magnetic behavior of a given grain. However, when the combined energy of all low energy pinning sites in a given grain is greater than 30 *kB·T*, then an AF-DW could be found pinned following those low energy pinning sites. The following parameters have been used for the simulation: *KAF*(293 K) = 8·106 erg/cm3, average grain size after crystallization 150 nm, standard deviation of the grain size distribution assumed to be lognormal 0.42, average value of the pinning strength at room temperature 30 *kB·T*, standard deviation of the distribution of pinning energies = 0.35, thickness of the AF layer 15 nm, defect concentration ~1% of the volume, the value of *υ0*=2.1·1012 Hz as measured by one of the authors32, grains simulated to ensure good statistics 104. The temperature dependence of the magnetocrystalline anisotropy is of the form (1-*T/TN*) where *TN*=690 K is the Néel temperature of the IrMn. The same temperature dependence was assumed for the pinning strength. We assumed that the contribution to the EB of a multidomain volume is 60% lower than that of single domain volume.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Acknowledgement**

We thank Prof. Kevin O’Grady for his helpful discussions. This work has been funded by the Spanish Ministerio de Economía y Competitividad through the projects MAT2014-52477-C5-1-P and MAT2014-52477-C5-3-P and by the Spanish Consejo Social of the Universidad Politécnica de Madrid through the scholarship "Ayuda del Consejo Social para el Fomento de la formación y la Internacionalización de Doctorandos", awarded for a three months internship at the University of York. VKL thanks the funding support by EPSRC grant EP/K03278X/1. J.C. and J.L.F.C. thank support by MINECO through Projects FIS2016-78591-C3-1-R and SEV-2016-0686 and by Comunidad de Madrid through Project S2013/MIT-2850.

**Author Contributions**

A.M. deposited the samples and performed (or was strongly involved) in most of the experimental characterization. T.H. performed some of the crystallization experiments observed using electron microscopy. M.M. designed some of the experimental set-ups used for characterizations. J.L.F.C. and J.C. provided expertise and performed Kerr microscopy with A.M. C.A. was the first to suggest that a phase transition in the IrMn was likely behind the unusual behavior of the samples. G.V.F. helped with the magnetic characterization following the York protocol and performed the fitting displayed in figure 4d. V.K.L. and B.K. performed the TEM characterization with some of the specimens measured by D.K. J.L.P. directed the research and designed the sputtering system used for the deposition of the samples. J.L.P. wrote the manuscript with inputs from all the authors.

**Competing financial interest**

The authors declare no competing financial interests.

**Figure Legends**

**Figure 1 | Structural and magnetic characterization of the samples. a**, Hysteresis loop of the sample just after being deposited (black) and 65 hours later (blue). The Exchange Bias developed spontaneously in only a few hours. **b**, XRD *θ*-2*θ* scans of the same sample taken every 1.5 h in between the measurements shown in **a**. The IrMn (111) texture develops during those hours. **c**, Area of the IrMn (111) peak shown in **b** versus time. The area increases with time following a sigmoidal function. The solid line is a fit to the Avrami model (see text) **d**, Sequence ofhysteresis loops with time in a twin sample to the one shown in **a**, **b** and **c** (each loop was taken in 20 min). The loop with black circles corresponds to a measurement performed only a few minutes after the sample was deposited by sputtering. The consecutive hysteresis loops show how the EB forms, progressively affecting a larger portion of the sample. The sample remains always at RT. **e**, Kerr image of the sample taken 8 hours after deposition, showing areas (lighter contrast – blue arrow) where the FeCo is exchanged biased, while other areas (darker contrast – yellow arrow) remain free. **f**, Kerr image of the sample taken 14 hours after deposition, showing how the exchange biased areas have grown to cover almost the entire sample. **g**, Evolution with time of the proportion of the hysteresis loop that shows exchange bias in **d**, which effectively represents the area of the sample that is exchanged biased (light contrast in the Kerr images), normalized to the total area of the sample. The black solid line is the best fit of the magnetic data following the Avrami model (see Supplementary Information) and the best fit for the structural data in **c** is superimposed witha red dashed line. Both the structural and the magnetic evolution show an almost identical behavior.

**Figure 2 | TEM and Selective Area Diffraction (SAD) paired images of a Ta/IrMn/Ta sample. a**, Magnetic structure of γ-IrMn3 phase, after Ref. 23. **b**, Magnetic structure of L12-IrMn3 phase after Ref.23. **c**, Plan-view Bright Field image (BF-TEM) of a specimen with the structure Ta(3)/IrMn(15)/Ta(5), taken soon after deposition, showing the nanocrystalline nature of the deposited IrMn, also confirmed by the SAD pattern in **e**. **d**, Plan-view TEM image from the same specimen hours later, in an area where the crystallization of the IrMn is taking place. Single crystal grains of (111) oriented IrMn develop, as confirmed by the SAD pattern in **f**. Note that superlattice diffraction spots from the L12-IrMn3 (red circles) are missing.

**Figure 3 | Influence of the FeCo layer on the IrMn phase transition. a**, BF-TEM image of a sample with no FeCo layer on top of the IrMn, showing a limited number of defects after the IrMn is fully crystallized. **b**,BF-TEM image of a sample with a FeCo layer on top of the IrMn, showing extended structural defects in the IrMn layer when fully crystallized. **c**, Atomic resolution HAADF-STEM image showing a grain antiphase domain boundary in the IrMn of the sample with the FeCo layer. **d**, BF-STEM image at the IrMn/FeCo interface in the vicinity of a stacking fault boundary.

**Figure 4 | Magnetic characterization after crystallization of the IrMn layer. a**, Sequence of hysteresis loops with time showing the decay of the EB field, *Heb*. The sample is kept at RT and saturated in the negative direction between measurements. **b**, EB field versus time during the reversal experiment. The inset shows the same data plotted against a logarithmic scale. **c**, Setting of the EB, following the annealing procedure described in Methods. The inset shows the hysteresis loop at selected setting temperatures. The annealing leads to an almost immediate decrease of the coercive field and to a decrease of the EB field for setting temperatures higher than 410 K. **d**, Estimation of the blocking temperature following the annealing procedure described in Methods. The coercive field remains constant during all the process. The solid line is the fitting using the AF-DW pinning model described in the text and in Methods.

**Figure 5 | Changing the direction of the magnetization in the FeCo layer as the crystalline phase of the IrMn layer develops.** The picture is a photograph taken with the Kerr microscope during the crystallization of the IrMn layer. The photograph has false colors to distinguish the regions with EB and their direction (green and blue) and the areas with free FeCo (yellow areas). The remanence of the FeCo has been switched twice during the crystallization, starting by up direction (inner blue in the annular domains), then down (green) and then up again (external blue areas). If the external field is not switched again, the blue outer area in the picture would keep spreading until it covers all the sample.