Origin of the anomalous temperature dependence of coercivity in soft ferromagnets

R. Moubah, M. Ahlberg, A. Zamani, A. Olsson, Shengwei Shi, Zhengyi Sun, S. Carlson, A. Hallen, B. Hjorvarsson and P. E. Jonsson

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

R. Moubah, M. Ahlberg, A. Zamani, A. Olsson, Shengwei Shi, Zhengyi Sun, S. Carlson, A. Hallen, B. Hjorvarsson and P. E. Jonsson, Origin of the anomalous temperature dependence of coercivity in soft ferromagnets, 2014, Journal of Applied Physics, (116), 5, 053906.

<http://dx.doi.org/10.1063/1.4892038>

Copyright: American Institute of Physics (AIP)

<http://www.aip.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-111284>

Origin of the anomalous temperature dependence of coercivity in soft ferromagnets

R. Moubah, M. Ahlberg, A. Zamani, A. Olsson, S. Shi, Z. Sun, S. Carlson, A. Hallén, B. Hjörvarsson, and P. E. Jönsson

Citation: [Journal of Applied Physics](#) **116**, 053906 (2014); doi: 10.1063/1.4892038

View online: <http://dx.doi.org/10.1063/1.4892038>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/116/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Magnetic interactions in FePt/soft magnetic underlayer double-layered structure observed by anomalous Hall effect](#)

J. Appl. Phys. **97**, 10N511 (2005); 10.1063/1.1852858

[Influence of ion implantation on the magnetic properties of thin FeCo films](#)

J. Appl. Phys. **97**, 073911 (2005); 10.1063/1.1875737

[Magnetic and structural characterization and ferromagnetic resonance study of thin film HITPERM soft magnetic materials for data storage applications](#)

J. Appl. Phys. **93**, 6528 (2003); 10.1063/1.1555871

[Soft magnetic properties of Co–Fe–Zr–B–Al–O films](#)

J. Appl. Phys. **91**, 8450 (2002); 10.1063/1.1447521

[Microstructural origin of soft magnetic properties of sendust films prepared by N₂ reactive sputtering](#)

J. Appl. Phys. **84**, 945 (1998); 10.1063/1.368159

A horizontal banner with an orange background and a white border. The text '2014 Special Topics' is centered in a large, white, sans-serif font. Below the text are five circular icons, each with a different background and text. From left to right: 1. A red and white geometric pattern with the text 'PEROVSKITES'. 2. A blue and white grid pattern with the text '2D MATERIALS'. 3. A green and white molecular structure with the text 'MESOPOROUS MATERIALS'. 4. A yellow and white molecular structure with the text 'BIOMATERIALS/ BIOELECTRONICS'. 5. A brown and white molecular structure with the text 'METAL-ORGANIC FRAMEWORK MATERIALS'. At the bottom left is the 'AIP | APL Materials' logo. At the bottom right is a red banner with the text 'Submit Today!' in white.

Origin of the anomalous temperature dependence of coercivity in soft ferromagnets

R. Moubah,¹ M. Ahlberg,¹ A. Zamani,¹ A. Olsson,¹ S. Shi,² Z. Sun,² S. Carlson,³ A. Hallén,⁴ B. Hjörvarsson,¹ and P. E. Jönsson¹

¹Department of Physics and Astronomy, Uppsala University, P.O. Box 516, SE-75120 Uppsala, Sweden

²Department of Physics, Chemistry and Biology, Linköping University, SE-58183 Linköping, Sweden

³MAX IV Laboratory, Lund University, SE-22100 Lund, Sweden

⁴KTH, School of Information and Communication Technology, Royal Institute of Technology, SE-16440 Kista-Stockholm, Sweden

(Received 9 April 2014; accepted 9 July 2014; published online 4 August 2014)

We report on the origin of the anomalous temperature dependence of coercivity observed in some soft ferromagnets by studying the magnetic and electronic properties of FeZr films doped using ion implantation by H, He, B, C, and N. The anomalous increase of the coercivity with temperature was observed only in the C- and B-doped samples. Using x-ray photoelectron spectroscopy, we show that the anomalous behavior of the coercivity coincides with the occurrence of an electron charge transfer for those implanted samples. The origin of the anomaly is discussed in terms of (i) magnetic softness, (ii) nature of the Fe-C and -B covalent bonds, and (iii) large charge transfer.

© 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892038>]

Magnetic properties can be tailored by mixing magnetic and non-magnetic elements.^{1,2} One of the most intriguing observations in this context is the abnormal enhancement of coercivity or magnetic anisotropy with increasing temperature in FeCo-Hf,³ FeCo-Zr,⁴ FeCo-B,⁵ or Fe-YB.⁶ Typically, the coercivity or magnetic anisotropy decreases with increasing temperature as a consequence of reduced exchange coupling and spin orbit interaction with increasing temperature.⁷ However, in two-phase systems, consisting of nanocrystallites randomly distributed in a magnetic amorphous matrix, the increase of coercivity with temperature has been observed close to the transition temperature of the soft amorphous phase.^{8–10} Also in other materials, controversial mechanisms^{11,12} and anomalies^{3–6} of the temperature dependence of the coercivity have been reported so far. From a fundamental point of view, it is important to understand how the anisotropy can be enhanced with increasing temperature. Furthermore, the control of the temperature dependence of coercivity is useful for potential applications where a good thermal stability of the coercivity is required, such as in spintronic or high frequency magnetic devices.

In this work, we investigate the effect of doping by H, He, B, C, and N on the magnetic and electronic properties of Fe₉₃Zr₇¹³ (FeZr) amorphous films. We observe an anomalous temperature dependence of the coercive field for the C- and B-implanted samples. X-ray photoelectron spectroscopy (XPS) indicates that a charge-transfer mechanism is involved only in the C- and B-implanted samples, while structural analyses using extended x-ray absorption fine structure (EXAFS) spectroscopy reveals that only the N-implanted sample is partly crystalline. Hence, the C- and B-implanted samples can be used for elucidating the origin of the anomalous temperature dependence of the coercivity in *single-phase* soft amorphous ferromagnets.

Amorphous FeZr films were prepared by using dc magnetron sputtering.^{14,15} The base pressure of the chamber was

below 9×10^{-10} millibar, and the operating pressure of Ar gas, with a purity of 99.9999%, was 2.7×10^{-3} millibar during growth. The films were grown on $10 \times 10 \times 0.5$ mm³ Si(001) substrates with a native oxide layer, which were annealed at 550 °C for 30 min prior to deposition, in order to clean the surface. A 5-nm-thick amorphous Al₇₀Zr₃₀ seeding layer, deposited from a compound target, was used to facilitate an amorphous growth of the FeZr layers.¹⁶ The FeZr layers with thicknesses of 40 nm were deposited at room-temperature using a compound target (99.9% purity). Each film was protected by a capping layer of Al₇₀Zr₃₀ (6 nm) to avoid oxidation of the magnetic layer in air. The implantation was performed *ex-situ* at room-temperature using an ion implanter. The ion energies were adjusted to have similar depth concentration profile for the different implanted elements and were 3, 5, 15, 18, 20 keV, for H, He, B, C, and N, respectively. For all samples, the ion dose was 4.75×10^{16} ion/cm², yielding films with average concentrations of around 11 at. % [(FeZr)₈₉X₁₁ (X=H, He, B, C, N)]. For more details on the implantation, see Refs. 14 and 15. Structural analysis were performed using EXAFS spectroscopy at MAX-lab in Lund, Sweden.¹⁷ Data were collected over the K edge of Fe using a Si(111) double-crystal monochromator and fluorescence mode with an energy-dispersive solid-state detector (Si Nano Technology Vortex). The resolution $\Delta E/E$ was 10^{-4} . The total time per scan was 50 min, and several data scans were averaged. Magnetization measurements were performed using magneto-optical Kerr effect (MOKE), with two setups for low and high applied magnetic fields, in the longitudinal geometry with s polarized light. X-ray photoelectron spectroscopy measurements were performed with a Scienta ESCA 200 spectrometer equipped with the monochromated Al K α source (1486.7 eV).¹⁸ The base pressure of the chamber was about 5×10^{-10} millibar. Ar⁺ etching was carried out in order to remove a few nanometers of the capping layer of the samples. The experimental

conditions were such that the full width at half maximum of the Au $4f_{7/2}$ line was 0.65 eV. The binding energies were calculated with an error of ± 0.025 eV. Different sets of XPS spectra were recorded, all showing reproducible results.

Fig. 1 shows k^2 -weighted EXAFS data for the as-grown and C-, B-, and N-implanted FeZr samples together with a reference sample of crystalline Fe. The EXAFS oscillations are lower in amplitude and die out faster at high k -values for an amorphous sample compared to a crystalline sample due to the Debye-Waller effect caused by structural disorder.¹⁹ It can be seen that the EXAFS spectra of the C and B-implanted samples are similar to the as-grown FeZr sample, all with low amplitudes of the EXAFS oscillations indicating that these samples are amorphous. Similar results were obtained for the H and He-implanted samples (data not shown here). On the other hand, the EXAFS spectra of the N-doped sample shows oscillations with higher amplitudes (but still lower than for the crystalline Fe reference sample), indicating that the FeZr-N sample is partially crystalline. As the heaviest of the dopants, the N ions are implanted with a higher energy than the other dopants, and crystallization is more likely to happen.

Figure 2(a) presents the change of the remanent magnetization as a function of temperature for as-grown H, He, B, C, and N implanted FeZr films. These curves show that all the films are ferromagnetic and that the T_C increases upon implantation, with a shift in T_C depending on the implanted elements as presented in Figure 2(b). We note that the T_C could not be directly determined for B- and N-implanted samples due to the limited temperature range available in the high field MOKE setup (380 K). The ordering temperature in those samples were, therefore, obtained by extrapolation of the $M(T)$ curves.

As shown in Figure 2(b), the T_C increases as the atomic radius of the implanted elements is increased, which can be reproduced by using the Bethe-Slater curve, where the exchange integral interaction increases as the Fe-Fe interatomic distance expands. The T_C of the N-implanted FeZr sample does not follow the linear trend of the ordering temperature with the atomic radius of the implanted element. Its

FIG. 1. k^2 -weighted EXAFS spectra recorded at 80 K and at the Fe K edge for crystalline Fe (used as a reference), as-grown FeZr film, and those implanted by B, C, and N.

FIG. 2. (a) Normalized remanent magnetization as a function of temperature for the as-grown FeZr film and those implanted by H, He, B, C, and N. The measurements were performed by making several hysteresis curves at fixed temperatures with the applied field parallel to the in-plane direction and deducing the remanent magnetization at each temperature. The normalization was made by dividing each data by the value of the remanent magnetization at 80 K. (b) The dependence of T_C as a function of the atomic radius of the implanted elements. The T_C of the N-implanted sample is a lower estimate.

T_C is higher than those of C- and B-implanted samples, although the atomic radius of N is smaller. This is due to the presence of crystallites, as identified by the EXAFS data.

The magnetization curves recorded at 80 K of the samples are plotted in Figure 3. The values of the coercive and saturation fields of the as-grown sample are higher than those of the implanted samples. The decrease of the coercive and saturation fields upon implantation are associated with the diminishing of the non-collinear ferromagnetism of the as-grown FeZr films¹³ due to less exchange frustration that drastically reduces the size of the energy barriers hindering domain wall motion, induced by the increase of the Fe-Fe interatomic distance.

In order to uncover the details of the effect of implantation by different elements on the electronic properties of the FeZr system, we have carried out XPS measurements at the Fe 3p core levels. In a recent report, we have studied the effect of implantation by C on the Fe 2p and 3p levels.¹⁵ However, only an increase of the peaks width of the Fe $2p_{3/2}$ and $2p_{1/2}$ levels has been observed upon implantation by C, and no shift in the binding energies was detected, indicating

FIG. 3. Magnetization curves at 80 K of the as-grown FeZr film and those implanted by H, He, B, C, and N. The magnetic field was applied parallel to the in-plane direction. The inset shows the hysteresis curve of the as-grown sample in a large field window.

that negligible electron charge transfer has occurred at the Fe 2p core levels. For an intra-atomic charge transfer, deeper core level peaks (Fe 2p) tend to be broad, and it is difficult to determine their shifts.²⁰ Nevertheless, shallow levels (Fe 3p) should provide a better sensitivity of the changes in the chemical-state.^{21,22} Thus, we choose to work at the Fe 3p core levels to characterize the charge transfer for different implanted samples. The spectra obtained at the Fe 3p core levels for as-grown and different implanted samples are presented in Figure 4(a). In order to compare them, the spectra have been normalized to the intensity of their main peak. For all cases, the implantation leads to the broadening of the Fe 3p core levels peaks. The increase of the peaks widths is caused by the changes in the chemical bonding induced by the incorporation of the implanted elements in the FeZr matrix modifying the nearest neighbor environment of the Fe atoms.

As presented in Figure 4(c), the Fe 3p levels of the C- and B-implanted samples are shifted to higher binding energies compared with that of the as-grown sample. The peak positions were determined using Gaussian fits and the deduced shifts are 0.26, and 0.61 eV for the B- and C-implanted samples, respectively. No shift in the binding energies can be detected for the other implanted elements (H, He, and N) [Figure 4(b)]. The shifts can be understood by the occurrence of a charge transfer from Fe to C, and B in the FeZr matrix.²³ The large shift in C is caused by its larger electron affinity: it is 1.2, 0.3, 0.05 eV for C, B, and N, respectively.²⁴ The electron affinity of H is 0.8 eV; the absence of charge-transfer in the case of H can be understood by the nature of the 1s orbitals, which is highly delocalized. Helium is inert, and, therefore, no charge-transfer is expected. These observations are in agreement with the calculations of Kong *et al.*²⁵ showing that the chemical bonds for Fe-H and Fe-N are metallic, whereas the Fe-C bond is covalent.

One can notice a shoulder that appears at low binding energies (49–51 eV) for the as-grown, H, and He implanted

FIG. 4. XPS spectra of Fe 3p core levels of (a) the as-grown FeZr film, and those implanted by H, He, B, C, and N. A zoom of the curves, showing the shift in the binding energies of the Fe3p core levels of B and C implanted films (b), and its absence for the H, He, N implanted films.

samples [Figure 4(a)]. Arranz *et al.*²⁶ have studied the Fe 3p components in pure Fe films for different deposition times, and attributed this feature to Fe surface atoms with a lower atomic coordination (outer atomic layer). The hybridization nature between the 2p orbitals of B, C, and N with Fe in the outer atomic layer may lead to the disappearance of this shoulder. The feature at low binding energies can also be assigned to the Zr 4s levels,²¹ however, the distinction between the Zr 4s and Fe 3p outer atomic layer levels is difficult.

The shifts in the binding energies observed in B- and C-implanted samples are accompanied by anomalies in the temperature dependence of the coercivity. Figure 5 shows the temperature dependence of the coercivity for the different samples. The as-grown, H, He, and N implanted samples exhibit a decrease of the coercivity with increasing temperature. The C- and B-implanted samples unveil an unusual increase of the coercive field with increasing temperature.

FIG. 5. The coercivity as a function of temperature for the as-grown FeZr films and those implanted by H, He, B, C and N. Inset: a zoom of the B-implanted sample curve, highlighting its anomalous temperature dependence of the coercivity. The measurements were done up to 300 K due to the limited temperature range available in the low field setup.

The unusual increase of coercivity with temperature for the C- and B-implanted samples coincide with the occurrence of an electron charge-transfer observed by XPS. The increase of temperature will lead to an increase of the charge-transfer as a result of the increase of the thermal energy, and thus, the coercivity increases. This explanation can be supported by the work of Enz *et al.*,²⁷ who have observed a significant increase of the coercivity in the *magnetically soft* Si-doped Yttrium Iron Garnet ($\text{Y}_3\text{Fe}_{6-x}\text{Si}_x\text{O}_{12}$) upon illumination. In that case, the increase of the coercivity was inferred to be caused by the electron charge-transfer induced by light illumination.²⁷ The B-implanted sample presents a slope change in the temperature dependence of the coercivity (inset of Figure 5), which is consistent with thermal processes becoming active with increasing temperature. We note that charge transfer enhanced coercivity has been reported in other systems.²⁸

The nature of the chemical bonds should also contribute to the abnormal behavior of the coercivity: For Fe-H and Fe-N, the bonds are metallic with a delocalized character. However, the Fe-C bond is covalent with a directional feature,²⁵ which increases the local magnetic anisotropy.²⁹ Thus, the local magnetic anisotropy increases as the temperature increases via charge transfer causing an increase of the coercivity. Using light illumination, Bettinger *et al.*³⁰ have demonstrated that charge-transfer enhanced ferromagnetism requires a small magnetic anisotropy in $(\text{MnZnFe})_3\text{O}_4$. This is also in agreement with the observation of an abnormal enhancement of the permeability with increasing temperature reported for the same material.³¹ When the magnetic anisotropy is small, the permeability is high, the effect of charge-transfer is large, and ferromagnetism is enhanced.³⁰ These observations are in line with our results since the films studied here are soft with very small coercivities: 1 and 0.17 mT for C- and B-implanted elements at 80 K, respectively. Therefore, the combination of magnetic softness, directionality of covalent bonds, and large charge transfer should all contribute to the enhancement of the coercivity with temperature. This scenario is consistent with the difference in the anomalous changes of coercivity as a function of temperature. The increase of the coercivity with

increasing temperature is more pronounced in the C-implanted sample compared to the B-implanted (Figure 5). This difference can be linked to the binding energies shifts [Figure 4(c)] (charge-transfer), which is bigger in the case of C, and smaller for the B element, and it is absent for the other implanted elements.

In summary, we have shown the link between the electron charge transfer and the abnormal behavior of the coercivity in single-phase implanted FeZr amorphous films. The key parameters for the anomaly are the magnetic softness, directional feature of covalent bonds, and large charge transfer. The anomalous enhancement of the coercivity with increasing temperature may be of future use in potential applications where a coercivity stability at high temperature is needed.

- ¹H. Miyasaka, N. Motokawa, S. Matsunaga, M. Yamashita, K. Sugimoto, T. Mori, N. Toyota, and K. R. Dunbar, *J. Am. Chem. Soc.* **132**, 1532 (2010).
- ²W. E. Broderick, J. A. Thompson, E. P. Day, and B. M. Hoffman, *Science* **249**, 401 (1990).
- ³N. N. Phuoc and C. K. Ong, *Adv. Mater.* **25**, 980 (2013).
- ⁴N. N. Phuoc and C. K. Ong, *Appl. Phys. Lett.* **102**, 212406 (2013).
- ⁵L. Yiping, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klabunde, *J. Magn. Magn. Mater.* **104**, 1545 (1992).
- ⁶A. V. Andreev, M. I. Bartashevich, T. Goto, and S. M. Zadvorkin, *J. Alloys Compd.* **262**, 467 (1997).
- ⁷H. B. Callen and E. Callen, *J. Phys. Chem. Solids* **27**, 1271 (1966).
- ⁸K. Suzuki and J. M. Cadogan, *Phys. Rev. B* **58**, 2730 (1998).
- ⁹A. Hernandez, P. Marín, M. Vázquez, J. M. Barandiarán, and G. Herzer, *Phys. Rev. B* **58**, 366 (1998).
- ¹⁰G. Herzer, *IEEE Trans. Magn.* **25**, 3327 (1989).
- ¹¹B. Staunton, S. Ostanin, S. S. A. Razee, B. L. Gyorffy, L. Szunyogh, B. Ginatempo, and E. Bruno, *Phys. Rev. Lett.* **93**, 257204 (2004).
- ¹²R. Skomski, O. N. Mryasov, J. Zhou, and D. J. Sellmyer, *J. Appl. Phys.* **99**, 08E916 (2006).
- ¹³D. H. Ryan, J. M. D. Coey, E. Batalla, Z. Altounian, and J. O. Strom-Olsen, *Phys. Rev. B* **35**, 8630 (1987).
- ¹⁴A. Zamani, A. Hallén, P. Nordblad, G. Andersson, B. Hjörvarsson, and P. E. Jönsson, *J. Magn. Magn. Mater.* **346**, 138 (2013).
- ¹⁵R. Moubah, A. Zamani, A. Olsson, S. Shi, A. Hallén, S. Carlson, D. Arvanitis, P. Nordblad, B. Hjörvarsson, and P. Jönsson, *Appl. Phys. Express* **6**, 053001 (2013).
- ¹⁶P. T. Korelis, A. Liebig, M. Björck, B. Hjörvarsson, H. Lidbaum, K. Leifer, and A. R. Wildes, *Thin Solid Films* **519**, 404 (2010).
- ¹⁷S. Carlson, M. Clausen, L. Gridneva, B. Sommarin, and C. Svensson, *J. Synchrotron Radiat.* **13**, 359 (2006).
- ¹⁸Y. Q. Zhan, X. J. Liu, E. Carlegir, F. H. Li, I. Bergenti, P. Graziosi, V. Dediu, and M. Fahlman, *Appl. Phys. Lett.* **94**, 053301 (2009).
- ¹⁹J. J. Rehr and R. C. Albers, *Rev. Mod. Phys.* **72**, 621 (2000).
- ²⁰J. J. Kolodziej, T. E. Madey, J. W. Keister, and J. E. Rowe, *Phys. Rev. B* **62**, 5150 (2000).
- ²¹D. Sangalli, E. Lamperti, E. Cianci, R. Ciprian, M. Perego, and A. Debernardi, *Phys. Rev. B* **87**, 085206 (2013).
- ²²M. J. Lee, S. J. Kang, J. Yoon Baik, K.-J. Kim, H.-D. Kim, H.-J. Shin, J. Chung, J. Lee, and J. Lee, *J. Appl. Phys.* **108**, 024507 (2010).
- ²³T. K. Sham, M. L. Perlman, and R. E. Watson, *Phys. Rev. B* **19**, 539 (1979).
- ²⁴C. Nordling and J. Österman, *Physics Handbook*, 8th ed. (Studentlitteratur AB, 2006).
- ²⁵Y. Kong, R. Zhou, and F. Li, *Phys. Rev. B* **54**, 5460 (1996).
- ²⁶A. Arranz, V. Pérez-Dieste, and C. Palacio, *Surf. Sci.* **521**, 77 (2002).
- ²⁷U. Enz, W. Lems, R. Etselaar, P. J. Rijniens, and R. W. Teale, *IEEE Trans. Magn.* **5**, 467 (1969).
- ²⁸B. Loukya, D. S. Negi, K. Dileep, N. Kumar, J. Ghatak, and R. Datta, *J. Magn. Magn. Mater.* **345**, 159 (2013).
- ²⁹E. Sjöstedt, L. Nordström, F. Gustavsson, and O. Eriksson, *Phys. Rev. Lett.* **89**, 267203 (2002).
- ³⁰J. S. Bettinger, R. V. Chopdekar, and Y. Suzuki, *Appl. Phys. Lett.* **94**, 072505 (2009).
- ³¹A. C. Razzitte, S. E. Jacobo, and W. G. Fano, *J. Appl. Phys.* **87**, 6232 (2000).