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INVESTIGATION OF POSSIBLE UNIAXIAL ANISOTROPY IN $Co_{11}Zr_2$ MAGNETIC PHASE

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ABSTRACT. The $Co_{11}Zr_2$ magnetic phase was obtained by a combination of melting, mechanical milling and high temperature annealing. The structure and magnetic properties of the obtained material were investigated. Even though the samples possessed low coercivity, it was shown that they possess uniaxial anisotropy.

Keywords*: hard magnetic materials, magnetic anisotropy, mechanical milling, high temperature annealing*

INTRODUCTION

Permanent magnets are crucially important for modern industry. The high energy product $Nd_2Fe_{14}B$ and highly stable $SmCo_5$ or Sm_2Co_{17} based magnets permit the creation of highly compact devices, such as mobile phones and laptops, while also being excellent at delivering high performance for large applications such as wind turbines and electric vehicles [1-6]. However, the supply of rare-earth elements is tenuous and their extraction and processing has significant environmental impact, therefore a concerted scientific effort has been put forward in recent years towards developing magnetic materials from non-rare earth elements [4]. Amongst the proposed solutions is the $Co_{11}Zr_2$ magnetic phase [7], as it has a promising magnetocrystalline anisotropy, excellent temperature stability and good corrosion resistance[8-10], the latter making it suitable for certain specific application where rare-earth based magnets would not fair as well [11].

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EXPERIMENTAL

The $Co_{11}Zr_2$ alloy was produced by induction melting pure elements under high purity Ar atmosphere. The produced ingot was placed in a tantalum boat and annealed at 1200 °C for 7 days, under high vacuum (10^{-6} mbar), in a Carbolite HVT 12/80/700 furnace, as described in the work used to produce the phase diagram [12]. The produced alloy was then crushed into powder and mechanically milled (MM) for 2 h in a Fritsch Pulverisette 4 planetary ball mill. The milling vials (80 ml) and balls (Ø = 15 mm) are made of 440C hardened steel. The ratio between the rotation speed of the disk and the absolute rotation of the vials was Ω/ω = 333 rpm/- 566 rpm with a ball to powder weight ratio of 10:1. The milled powder was then re-annealed at 1200 °C in the same conditions as the bulk ingot.

Crystalline structure of the produced material was investigated using X-ray diffraction, on a Bruker D8 Advance diffractometer equipped with a Cu source. The structure was refined using the Fullprof software, with only space group and unit cell parameters, as the atomic positions are still debated in the literature. The microstructure of the sample was investigated by scanning electron microscopy (SEM), on a Hitachi SU8230, while the soichimotery of the samples was checked by Energy Dispersive X-Ray Spectroscopy (EDX) on the same device.

For magnetic measurements the powders were blocked in epoxy and left to set in a homogenious applied magnetic field of 0.2 T until fully hardened. Thus two samples were produced, one with grains aligned along and one perpendicular to the applied field direction. An isotropic sample, left to harden in zero field, was also produced for reference.

The magnetic measurements were carried out using a vibrating sample magnetometer in a temperature range of 6 K to 300 K and in applied fields of up to 6 T.

First order reversal curves (FORC) were measured on the isotropic sample, at room temperature with a reversal (H_{rev}) and applied field (H_{app}) step of 0.01 T, from -0.5 to 0.5 T as the hysteresis loop fully closes at these fields. For the calculation of the FORC the program DoFORC [13] was used.

The FORC distribution is defined as the mixed second derivative of the first order reversal curves:

$$\rho_{FORC} = -\frac{1}{2}\frac{\partial^2 m_{FORC}(H_{rev}, H_{app})}{\partial H_{rev}\partial H_{app}} \quad (1)$$

where *m* is the magnetization.

The temperature dependence of the anisotropy constants was determined by the Sucksmith-Thompson method [14]:

$$\frac{\mu_0 H_{app}}{M_\perp} = \frac{2K_1}{M_s^2} + \frac{4K_2}{M_s^4} M_\perp^2 + N_D \quad (2)$$

where μ_0 is the magnetic permeability of vacuum H_{app} is the applied magnetic field, $M_\perp$ is the magnetization for the perpendicular aligned sample, K_1 and K_2 are the first and second anisotropy constants, M_s is the saturation magnetization and N_D is the demagnetization factor, measured as the slope (in the magnetization curve) at low field for the parallel oriented sample.

RESULTS AND DISCUSSION

The structure of the $Co_{11}Zr_2$ sample was refined using the orthorombic structure, space group Pcna. The results of the fitting as shown in ***Fig. 1***, the obtained lattice parameters were a=4.83(2) Å, b=8.178(6) Å and c=32.9(2) Å, values in agreement with the current state of the art, cited in the literature [9].

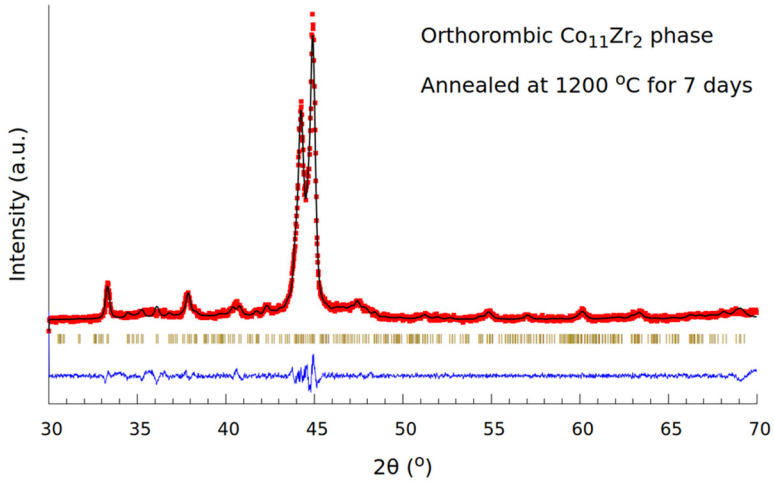

Fig. 1. *Rietveld refinement for $Co_{11}Zr_2$ annealed at 1200 °C for 7 days, with orthorhombic structure. XRD pattern red point, fit black line, reflection position olive bar. The difference between the XRD pattern and calculated structure is given as the blue line (below)*

The fit in ***Fig. 1*** was made using only the structure factor for the $Co_{11}Zr_2$ orthorombic phase, as the atomic positions are not yet known in the literature. Therefore the large peak around 45 deg could be convoluted with Co. As such, the rafinament was repeated with the addition of the Co phase, and the maximum possible Co content was determined to be 3%, an amount comparable to the error of determination. However, the XRD analysis is good enough to exclude the $Co_{23}Zr_6$ and $Co_{11}Zr_2$ romboedral [15] phases.

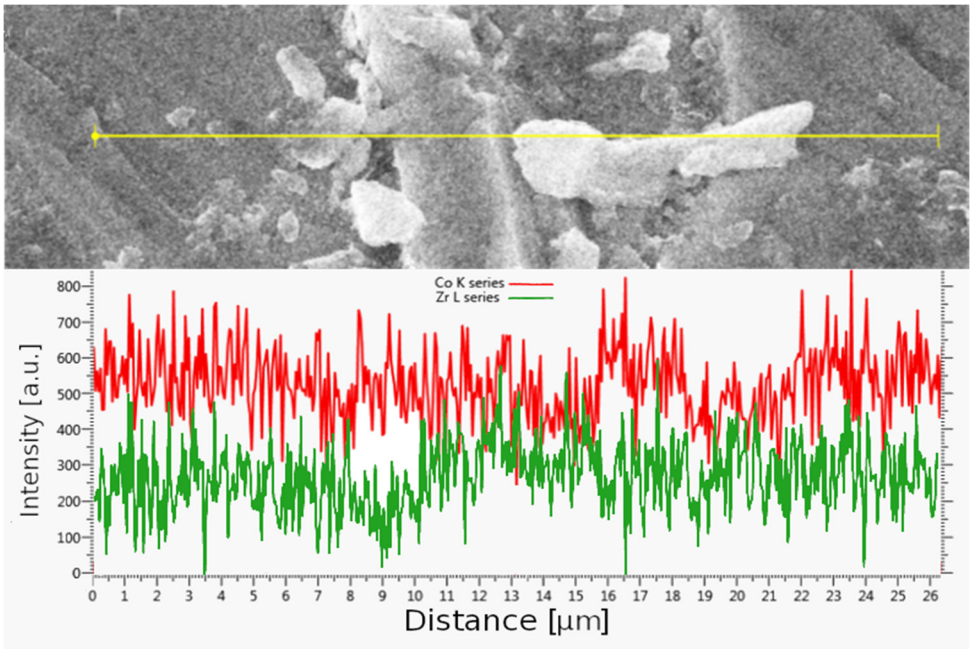

Figure 2. *SEM image and corresponding EDX line scan data (for Co and Zr) of investigated region*

The EDX analysis showed that the stoichiometry of the material is that of the $Co_{11}Zr_2$ phase, while line scans, selected image shown in

Figure 2, prove that the ratio between the two constituent elements does not vary significantly through the material.

First order reversal curves, measured at 300 K, show that the isotropic sample is a rather soft magnetic material. Most reversal processes take place very close to the reversible axis. The maximum reversal is centered around 0 T, the samples themselves showing a coercive field at 300 K of just 0.01 T.

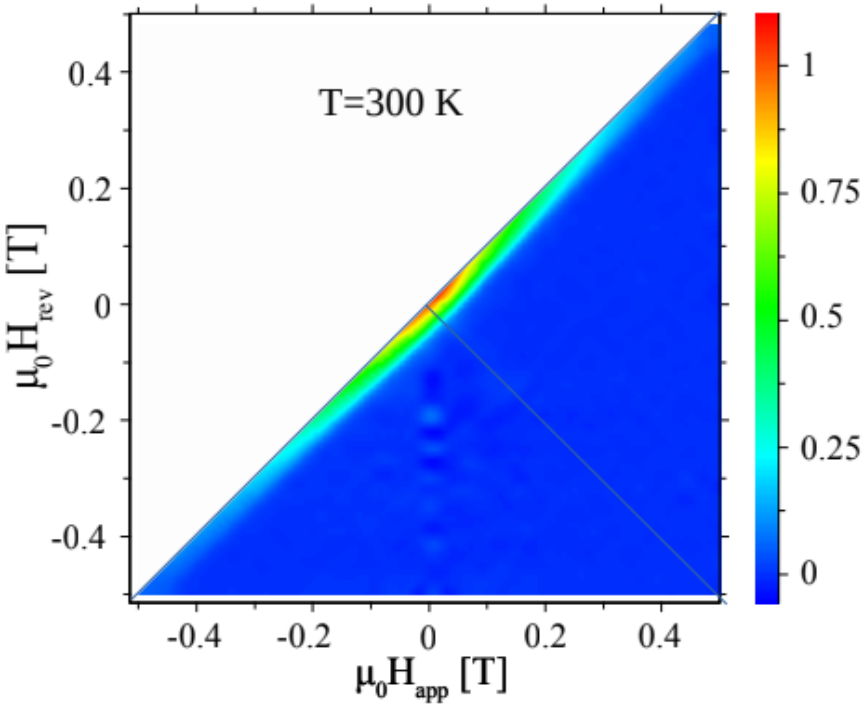

Figure 3. *FORC distribution for $Co_{11}Zr_2$ alloy recorded at room temperature*

Magnetization measurements were also carried out on the aligned samples, between 6 K and 300 K,

Figure 4a. These measurements indicate that although the samples are not fully aligned, the curves are not straight lines, there are significant and systematic differences between the magnetization curves of the parallel and perpendicular aligned samples, from low temperature to room temperature. Therefore, using the Sucksmith-Tompson method, the anisotropy constants were determined, shown in

Figure 4b. While the values of both parameters are low (very likely due to the significant misalignment present in the samples) both anisotropy constants are positive which is a strong indicator of uniaxial anisotropy.

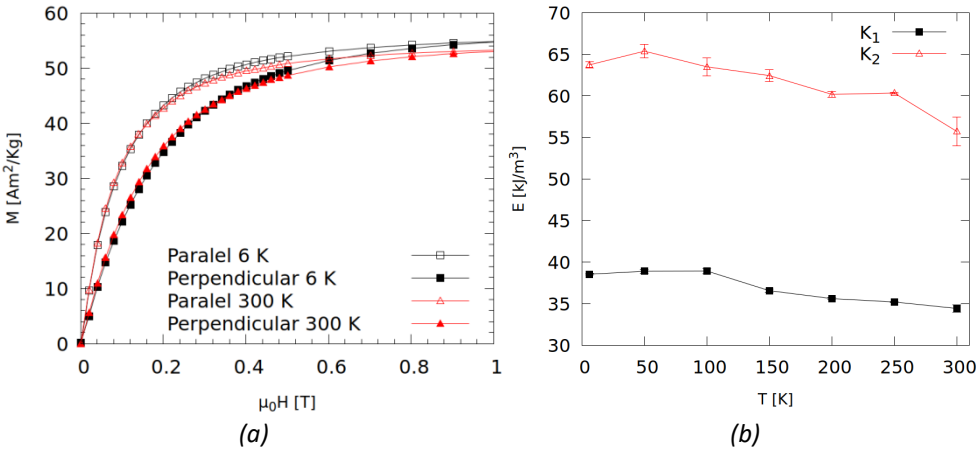

***Figure 4**. Magnetization measurements on aligned (parallel and perpendicular) $Co_{11}Zr_2$ samples (a) and anisotropy constants as a function of temperature (b).*

CONCLUSSIONS

The $Co_{11}Zr_2$ magnetic phase was successfully obtained by a combination of induction melting mechanical milling and high temperature annealing. The magnetic properties of the alloy were investigated and the evolution of the magnetocristalline anisotropy was studied in a temperature range between 6 and 300 K. The value of the uniaxial anisotropy energy for the magnetic phase was found to be very stable up to room temperature, the total anisotropy energy dropping by only 15% between 6 and 300 K.

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REFERENCES

1. D. Sander, S. O. Valenzuela, D. Makarov, C. H. Marrows, E. E. Fullerton, P. Fischer, J. McCord, P. Vavassori, S. Mangin, P. Pirro, et al. *J. Phys. D. Appl. Phys.* 50 (2017), doi:10.1088/1361-6463/aa81a1
2. J. M. D. Coey, *IEEE Trans. Magn.* 47, 4671-4681, (2011) doi:10.1109/TMAG.2011.2166975
3. D. Goll, H. Kronmüller, *Naturwissenschaften* 87, 423-438, (2000), doi:10.1007/s001140050755
4. J. M. D. Coey, *Engineering* 6, 119–131, (2020) doi:10.1016/j.eng.2018.11.034
5. N.T. Nassar, X. Du, T.E. Graedel, *J. Ind. Ecol.* 19, 1044–1054, (2015) doi:10.1111/jiec.12237
6. K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, *J. Clean. Prod.* 51, 1–22, (2013) doi:10.1016/j.jclepro.2012.12.037
7. T. Ishikawa, K. Ohmori, *IEEE Trans. Magn.* 26, 1370-1372, doi: https://doi.org/10.1109/20.104381
8. X. Zhou, J. Zhang, X. Liao, J. He, K. Li, Z. Liu J. Magn. Magn. Mater, 501, 166483, (2020) doi: https://doi.org/10.1016/j.jmmm.2020.166483
9. Z. Li, W.Y. Zhang, D.J. Sellmyer, X. Zhao, M.C. Nguyen, C.Z. Wang, K.M. Ho, *J. Alloy. Compd.*, 611, 167-170, (2014) doi: https://doi.org/10.1016/j.jallcom.2014.05.072
10. S. Manjura Hoque, S.K. Makineni, A. Pal, P. Ayyub, K. Chattopadhyay, J. Alloy. Compd., 620, 442-450, (2015), doi: http://dx.doi.org/10.1016/j.jallcom.2014.09.104
11. Y. Ouyang, R. Qiu, Y. Xiao, Z. Shi, S. Hu, Y. Zhang, M. Chen, P. Wang, *Chem. Eng. J*. 368, 331-339, (2019), doi: https://doi.org/10.1016/j. cej.2019.02.126
12. X.J. Liu, H.H. Zhang, C.P. Wang, K. Ishida, *J. Alloy. Compound*, 482, 99-105, (2009), doi:10.1016/j.jallcom.2009.04.032
13. D. Cimpoesu, I. Dumitru, A. Stancu*, J Appl Phys*, 125, 023906 (2019), doi: 10.1063/1.5066445
14. W. Sucksmith, J.E. Thompson, *Proc. R. Soc. London, Ser.* A 225, 362, (1954)
15. X. Zhao, L. Ke, M. C. Nguyen, C-Z. Wang, K-M. H, *J. Appl. Phys*. 177, 243902 (2015), doi: http://dx.doi.org/10.1063/1.4922984