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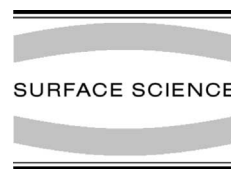
The influence of reversible adsorption of water molecules on the domain wall dynamics in amorphous ferromagnets

V.E. Zubov, A.D. Kudakov *, N.L. Levshin, T.S. Fedulova

Department of Physics, M.V. Lomonosov State University, 119899 Moscow, Russian Federation

Abstract

The influence of weakly adsorbed molecules on the 180° domain wall (DW) dynamics in the near-surface region of amorphous ferromagnets of composition $Fe_{76.5}Cu_1Nb_3Si_{13.5}B_6$ is observed by the magnetooptical method at room temperature. The high deceleration of an oscillating DW in the near-surface region and the decrease of the relaxation frequency from 10 to 4 kHz is observed for the pressure of water vapour in the range of 400–1300 Pa. The effect is explained by the influence of surface magnetic defects, caused by pressure on the micropore's walls located on the surface of ferromagnets. The pressure is induced by H-bond adsorbed clusters of water molecules. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Correlation between the adsorption–desorption processes and magnetic properties of ferromagnets was mentioned in the literature [1–4]. The investigation of oscillations of 180° domain wall (DW) in iron whiskers was carried out in the article [2]. Whiskers are samples with perfect crystal structure in the volume and at the surface. There is more than 10 times increase in the relaxation frequency of DW in the near-surface region if the air pressure decreases from atmospheric ($p = 100$ kPa) to $p = 1$ kPa in the vacuum cell, where the sample under study was placed. The effect was explained by the interaction of the DW with magnetic defects, caused by adsorption of molecules in the air.

The density of the crystallographic defects on surface of iron whiskers is low and their influence on the DW motion is insignificant (see Refs. [5,6] for details).

The possibility of observing such a weak effect as influence of reversible adsorption at room temperature on the DW mobility is explained by very low coercive force of the DW in iron whiskers (coercive force is equal to ∼0.1 A/m [6]). Coercive force in the best samples of soft amorphous magnets approaches to the above given values. At the same time amorphous magnets has complicated surface that is in particular characterized by macro and micropores. Thus amorphous samples are exact antithesis to iron whiskers with respect to the surface quality.

In this work we investigate the influence of reversible adsorption of water, oxygen, nitrogen and argon molecules at room temperature on the 180° DW mobility in amorphous ribbons.

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* Corresponding author.
  E-mail address: kudakov@magn.phys.msu.su (A.D. Kuda-kov).

2. Samples and experimental procedure

The investigated amorphous ferromagnetic samples of composition $Fe_{76.5}Cu_1Nb_3Si_{13.5}B_6$ were obtained by the spinning technique. Before amorphization, the melt was subject to special time–temperature treatment to obtain a uniform distribution of doping elements and, as a result, an improvement of the soft magnetic properties of the alloy [7]. The amorphous structure of the ribbons was established with the help of X-ray structural analysis. Samples were 25–30 μm thick, 0.55 mm wide and 15–20 mm long. Hereinafter the results of the experiments are described by using the co-ordinate system with x-axis and y-axis being directed along the sample width and length, and the direction of the z-axis corresponds to the shortest dimension. For the investigation samples were selected in the centre of which a 180° DW was situated, thus dividing each sample into two domains with the magnetization collinear to the y-axis. The effective width of the DW at the surface and the coercive force of the DW were determined by the magnetooptical method and proved to be equal to 7 μm and 1 A/m, respectively. The repeatable results were observed in the experiments with a lot of samples. The samples have a rough surface. The relief of the surface was clearly visible by optical microscope. Hence we can conclude, that the roughness factor (ratio of surface available for adsorption to the geometrical surface area) of amorphous ribbon is not less than roughness factor of the silver film (∼50) sprayed on the polished quartz substrate, which was investigated by one of the authors in Ref. [8].

The surface properties of the DW were investigated by a magnetooptical micromagnetometer described in the article [9]. The equatorial Kerr effect (EKE) was measured, which was caused by change in magnetization of illuminated part of the sample's surface through the DW motion in AC magnetic field. The slit of the photoelectron multiplier scanned along the x-axis perpendicular the DW direction. Magnetization of the sample is caused by DW motion in the external magnetic field H_y, directed along the y-axis, with an amplitude of 80 A/m in the frequency range of 20 Hz–15 kHz. The micromagnetometer allowed the inves-

tigations of DW dynamics in the near-surface region which thickness was determined by the penetration depth (approximately 0.01 μm) of used light. The micromagnetometer was supplemented with a vacuum cell, where the sample was placed, and the control system of gas flooding. The pressure of gas (p) in the cell can be changed from atmospheric till 10^{-3} Pa. In our experiment adsorption of molecules from the gas phase is realized on the real sample's surface, which is formed after a long duration of amorphous ferromagnets in the air. The sample was vacuumized before the gas flooding. In these conditions the thin oxide layer exists on the sample surface, covered with OH groups and H_2O molecules, adsorbed by co-ordination mechanism [10].

The frequency dependencies of DW oscillation amplitude (Δ) were investigated in atmospheres of different gases. As adsorbates there were picked molecules of water, oxygen and nitrogen, which are present in the air, and molecules of inert gas argon. The dependence of $\Delta(f)$ was characterized by relaxation frequency f_r, which is determined as $\Delta(f = f_r) = 0.7\Delta_0$ where Δ_0 − value of Δ if $f \rightarrow 0$.

The DW dynamics in the volume of samples was investigated by induction-type method. A measuring coil was wound on the sample for this purpose. A signal from this coil is proportional to magnetization of the sample. Magnetization of the sample is proportional to displacement of DW.

3. Results and discussion

Fig. 1 presents the dependencies of the EKE $\delta(x)/\delta_{max}$ in the amorphous ribbon, caused by the DW motion at different frequencies of external magnetic field. The oscillation amplitude of DW is determined as the width of EKE curves minus the width of the DW. Fig. 2 demonstrates the dependencies of the DW oscillation amplitude on the frequency of external magnetic field under the water molecules adsorption. Curve 1 corresponds to the pressure range of 1–400 Pa and its relaxation frequency is $f_r = 10$ kHz. The relaxation frequency decreases essentially when the pressure of water vapour increases (curves 2 and 3). The observed effect is completely reversible – the initial
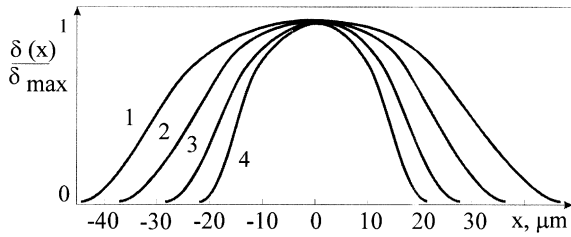
Fig. 1. Distributions of the EKE $\delta(x)/\delta_{max}$ caused by the oscillations of a 180° DW in magnetic field H_y with an amplitude 80 A/m at different frequencies. Curves 1–4: $f = 20$ Hz, $f = 2$ kHz, $f = 10$ kHz, $f = 15$ kHz.
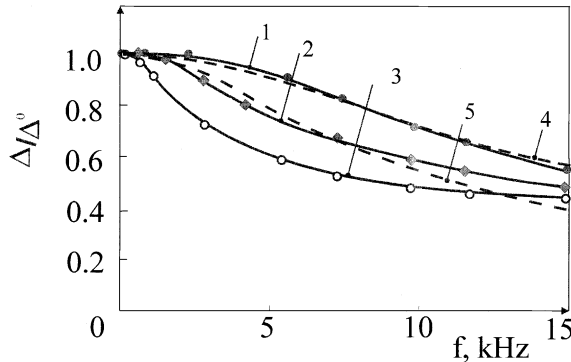

Fig. 2. Experimental dependencies of oscillation amplitude of the DW on magnetic field frequency when the water molecules adsorption takes place. Pressure of water vapour: curve 1: $p = 1$–400 Pa; 2: $p = 1000$ Pa; 3: $p = 1900$ Pa. Curves 4 and 5: theoretical dependencies $\Delta(f)$ for $f_r = 10$ and 6.5 kHz, respectively.
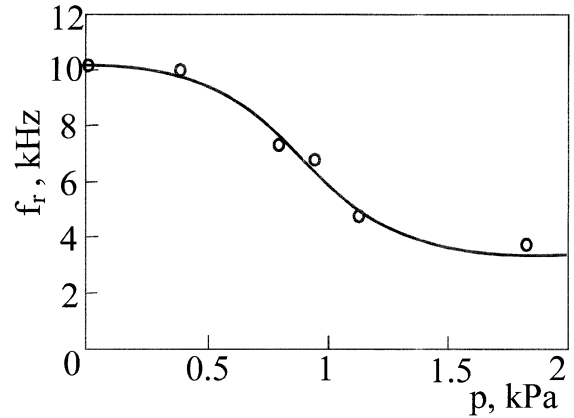

Fig. 3. Dependence of the DW relaxation frequency f_r on the water vapour pressure in the cell. The curves demonstrated on Fig. 2 and the method described in Section 2 were used to get the experimental points.

dependence of $\Delta(f)$ restores with the vacuumization of the sample. Significant change of the relaxation frequency f_r is observed at the pressure in the range of 400 Pa $< p <$ 1300 Pa (see Fig. 3). The oxygen, nitrogen and argon flooding into the vacuum cell with the near-atmospheric values of pressure did not change the dependence of $\Delta(f)$. The investigation of DW oscillations in the volume, which was realized by induction-type method, revealed the permanence of DW oscillation amplitude in the range of 20 Hz–15 kHz and its independence of gaseous atmosphere around.

The relaxation frequency of DW characterizes the value of the effective force of friction acting on the moving DW. Really, in our case the DW motion in AC magnetic field $H = H_0 \cos 2\pi ft$ may be

described with the help of harmonic oscillator equation. The term containing the DW effective mass is negligible in this equation

$$b\dot{x} + kx = 2I_sH, \qquad (1)$$

where: b – constant of viscous resistance, k – constant of the effective restoring force, caused by the demagnetizing field of a sample, I_s – saturation magnetization of a sample, $x(t) = \Delta \cos(2\pi ft - \varphi)$ – DW displacement from the equilibrium position, φ – phase difference between the external field and DW oscillations. It may be received the next relation for the amplitude of the DW oscillations:

$$\frac{\Delta}{\Delta_0} = \left[1 + \left(\frac{f}{f_r}\right)^2\right]^{-1/2}, \qquad (2)$$

where

$$\Delta_0 = \Delta(f = 0) = \frac{2I_sH_0}{k}, \quad f_r = \frac{k}{2\pi b}.$$

The obtained experimental curves in Fig. 2 qualitatively agree with the theoretical curves received with the help of Eq. (2) (see curves 4, 5 in Fig. 2). Both experimental and theoretical curves have a horizontal part at the low frequencies. The length of this horizontal part decreases when the pressure of water vapour increases and when the relaxation frequency decreases. This fact argues that the

observed decrease of relaxation frequency is associated with the increase of the viscous resistance constant in Eq. (1). More slow decrease with frequency of an experimental curve 2 in comparison with the theoretical curve 5 on Fig. 2 may be explained by influence of volume part of DW on the DW dynamics in the surface region. We did not take into account this fact in Eq. (2). Since the adsorption did not influence on dynamics of DW in the volume of the sample, so the observed effect was connected with formation of magnetic defects on the sample surface, which were caused by adsorption.

The samples were not exposed to preliminary purifying before investigations, so the sample's surfaces were covered with chemisorbed oxygen atoms, OH groups and coordination-bond H_2O molecules. They stay bounded with the surface when the sample is vacuumized. In these conditions all active centres located on the surface were occupied by chemisorbed molecules, and new strong chemical binding with absorbents in use is not possible. The observed reversible adsorption–desorption process correspond to formation and destruction of weak H-bonds between water molecules and hydrate cover on real sample's surface. Study of adsorption isotherms of molecules in gaze phase on different oxides has shown that quantity of adsorbed molecules is weakly depend on oxide composition [10]. That is why to estimate the quantity of adsorbed molecules one can use the isotherms of adsorption of the same adsorbates on the another adsorbents. It was found by the NMR spectroscopy at the silicon surface, that at the high degree of completing of the surface adsorbed water molecules from clusters with the thickness up to three layers of molecules, fastened on the coordination-bond H_2O molecules [10]. It is natural assumption that similar situation is realized at the hydrated surface of the amorphous ribbons.

The main change of the relaxation frequency f_r was observed for the pressure of water vapour varying from 0.4 to 1.3 kPa. It is observed that overlapping of the nearest water clusters adsorbed on the surface by the H-bond mechanism takes place in this range according to the isotherms of water adsorption for different oxides [10]. At the pressure of $p \sim 1.3$ kPa clusters merge together and

the polymolecular cover of the surface is formed by H_2O molecules. The amorphous ferromagnetic samples possess complicated surface characterized by the micropores in particular. Thus the mechanism of influence of the water molecules adsorption on the DW motion in the investigated samples can be explained as follows. At the pressure of water vapour in the range of $0.4 < p < 1.3$ kPa micropores are completed by the adsorbed water molecules. As a result the pressure on the micropores' walls arises that is caused by adsorbed water. These microstrains lead to existence of magnetic microdefects because of the magnetoelastic interaction. The proposed model of formation of the adsorption magnetic defects is shown in the Fig. 4. The effect is intensified due to the fact that the magnetoelastic energy constants for surface atoms are higher than for atoms in volume because of lower surrounding symmetry of the surface atoms [11]. Sizes of microspores involved in generating of the magnetic microdefects are determined by the merging of clusters of water molecules. These clusters adsorbed on the opposite sides of micropores' walls compose approximately six layers of water molecules. Whereas the investigated DW width is some orders wider than the typical sizes of the microdefects, the deceleration of the moving DW is determined by the fluctuations of microdefect's density. Adsorption of O_2, N_2 and Ar molecules at the room temperature is insignificant because of these molecules are connected to the real surface of magnets by the weak Van der Waals bonds. In this case significant
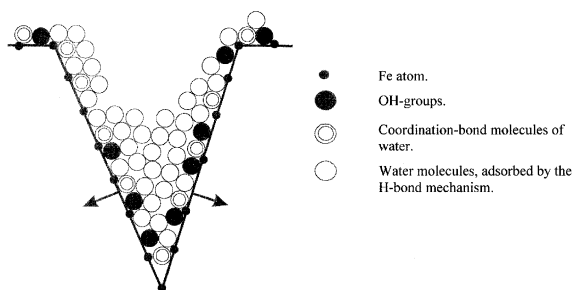

Fig. 4. The model of adsorption magnetic defect formation on the rough surface of amorphous ribbon which is caused by the hydrostatic pressure of adsorbed molecules on micropores' walls when the density of adsorbed molecules is high.

deformations of the sample surface caused by adsorption do not take place.

4. Conclusion

The reversible adsorption of weakly sorbed water molecules influences the dynamical properties of DW in near-surface region of the amorphous ferromagnets: the relaxation frequency of DW several times decreases due to the adsorption.

Mechanisms of influence of water molecules adsorption on the DW motion are different for smooth and rough surfaces. This is confirmed by the fact, that on the smooth surface of iron whiskers the relaxation frequency so high ($f_r > 50$ kHz) that cannot be measured due to the skin-effect influence. Furthermore, the effect of relaxation frequency decreasing in iron whiskers appears when the amount of adsorbed water molecules is of the order of a few tenths of monolayer [2]. On the rough surface of amorphous ribbons in contrast to the whiskers the DW deceleration is observed in vacuum, and most quick change of f_r appears when the adsorbed water molecules quantity is more than one monolayer. This conclusion is in accordance with well-known fact that the surface is contracted when the quantity of adsorbed water molecules is equal a few tenths parts of monolayer, and the surface is stretched when the quantity of adsorbed water molecules is more than one monolayer [10].

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