05,08

Magnetocaloric effect in the Fe/FeAl/Fe structure

© I.Yu. Pashenkin[1], N.I. Polushkin[1], M.V. Sapozhnikov[1,2], D.A. Tatarskiy[1,2], A.A. Fraerman[1]

[1] Institute of Physics of Microstructures, Russian Academy of Sciences,
Nizhny Novgorod, Russia
[2] Lobachevsky State University,
Nizhny Novgorod, Russia

E-mail: pashenkin@ipmras.ru

Received April 18, 2024
Revised April 18, 2024
Accepted May 8, 2024

The magnetocaloric properties of a thin FeAl(5) layer between strong Fe ferromagnets in the layered system Cr(50)/CoSm(30)/Fe(1)/Fe_xAl_{1-x}(5)/Fe(5)/Ta(5) ($x = 0.55$) have been studied experimentally. An increase in the magnetcaloric efficiency $\Delta S/\Delta H$ is expected in such structures (ΔS is the change in magnetic entropy, ΔH is the magnitude of the applied magnetic field), due to the exchange coupling at the interfaces between the interlayer and the surroundings. $\Delta S/\Delta H$ values have been determined from measurements of magneto-optical rotation curves using Maxwell's relation. A sharp increase in this parameter is discovered when the measurement temperature is increased to $T^* = 400$ K. A further increase in temperature above T^* led to destruction of the structure due to mixing of the layers. As the Fe concentration in the interlayer decreased below the value $x = 0.55$, the magnetization of the interlayer and the T_C value in it strongly decreased.

Keywords: magnetocaloric effect, magnetic heterostructures, exchange at interfaces, Curie temperature.

DOI: 10.61011/PSS.2024.07.58969.32HH

1. Introduction

The magnetocaloric effect (MCE) represents a temperature change in a magnet exposed to the outer magnetic field with variation of this field. The variation of magnetic entropy ΔS of a material during its adiabatic magnetization or demagnetization is the core process of this effect. The valueΔS is a magnetocaloric potential. Study of MCE in magnetic materials is reasonable from both fundamental and application points of view. MCE may provide an information on magnetic phase transitions and spin structures. Practical interest to MCE is related, generally, to the possibility of its using in energy-efficient and environmental friendly magnetic refrigerators. Moreover, MCE may be used in one of the methods for treating malignant tumors — method of hyperthermia [1]. Both of these applications have high requirements to the magnetocaloric efficiency $\Delta S/\Delta H$ (ΔH — variation of outer magnetic field) of materials used.

The characteristic temperature variations of the most well-known magnetocaloric materials are about 10 K and obtained by applying a magnetic field of several tesla to the ferromagnetic materials at near Curie temperature (T_C) [2,3]. Such fields can generally be produced using bulky magnets, which are undesirable for magnetic cooling [4,5]. This is one of the reasons to find the ways of increasing the magnetocaloric efficiency to decrease the magnetic field intensity necessary for functioning of the perspective devices. The authors of paper [6] suggested a brand new approach to increase the efficiency of magnetic cooling based on the use of magnetic neighbor effect of a „weak" ferromagnetic material (PM) with „strong" ferromagnets (FM) in thin-film nanostructures $FM_1/PM/FM_2$. The „weak" and „strong" ferromagnetic materials mean the ferromagnets with various T_C in case if T_C for the weak ferromagnet is within the study temperature range, and T_C for the strong ferromagnet is higher than this range. Due to exchange interaction in PM and FM boundaries, the average magnetization of PM layer will depend on mutual orientation of FM margins, that can be controlled by applying a relatively small outer magnetic field of 10^{-2} T. This method of measuring the magnetization (entropy) of a „weak" ferromagnet becomes more efficient with the ferromagnet thickness decrease, and $\Delta S/\Delta H$ may then reach huge values [6–8]. Paper [9] outlines an experiment demonstrating the actual possibility of exchange enhancement of the magnetocaloric efficiency of Gd layer in CoFeB/Fe/Gd/Fe/CoSm structures. However, such system doesn't allow a transfer to a 3D-material capable of cooling of real-world objects. A theoretical 3D-material with a magnetocaloric effect exchange enhancement may represent the particles of a „strong" ferromagnet placed in the „weak" ferromagnet matrix which will be magnetized by the exchange fields when all ferromagnetic particles have proper ordering due to applied magnetic field.

This paper describes an experimental study of magnetocaloric efficiency of $Fe_{0.55}Al_{0.45}$ alloy as a part of the multi-layer Fe/FeAl/Fe/CoSm nanostructure. The interest to binary alloy FeAl is explained by the fact that under certain conditions this alloy is capable of ordering making a superstructure [10,11]. While the most ordered alloy FeAl has lower Curie temperature compared to a disordered alloy. Paper [11] describes a possibility of using ionic emission to form local disordered ferromagnetic areas of the initial paramagnetic ordered FeAl film. This circumstance opens

new capabilities of getting a heterogeneous 3D-material with improved magnetocaloric properties due to the magnetic proximity effect. Development of such material, probably, will require a vast amount of studies including selection of ions energy and weight, required radiation doses, as well as geometry of the areas exposed to radiation. Such studies are associated with some technical difficulties and sufficient time periods. Therefore, prior to getting started with design of such a magnetocaloric 3D-material based on FeAl binary alloy, its magnetocaloric properties in Fe/FeAl/Fe/CoSm film system have been studied as earlier with Gd structures [9].

2. Experiment

The studied multilayer nanostructure Cr(50)/CoSm(30)/Fe(1)/$Fe_{0.55}Al_{0.45}$(5)/Fe(5)/Ta(5) (thicknesses are given in nm) (Figure 1) was grown by method of magnetron sputtering at room temperature on ATC2200-V device (AJA International Inc.). Residual pressure in the growth vessel didn't exceed $7 \cdot 10^{-8}$ Torr. The layer CoSm(30)/Fe(1) (FM_2) performs the function of a secured layer. Cr sub-layer is necessary to provide magnetic hardness CoSm. The layer Fe(5) (FM_1) is free and can be re-magnetized in relatively small magnetic fields. Sub-layer $Fe_{0.55}Al_{0.45}$(5) (PM) plays a role of „weak“ ferromagnet or „refrigerant“ The layer Ta(5) protects the structure from oxidation. Thus, in the obtained structure the states with co-directional and opposite directional mutual orientation of magnetization of „strong“ ferromagnets and, respectively, efficient exchange fields impacting the „weak“ ferromagnet FeAl (PM) can be implemented.

Magnetic and magnetocaloric properties of the fabricated structure were studied by the method of magneto-optic Kerr effect. The curves of magneto-optical rotation were received under various temperatures in the range from 295 to 398 K in magnetic field applied in the plane of the sample. The magnetocaloric potential of FeAl interlayer was assessed using Maxwell relationship.

$$\Delta S = \int_{H_{\uparrow\uparrow}}^{H_{\uparrow\downarrow}} \left(\frac{\partial M(H,T)}{\partial T} \right) dH. \qquad (1)$$

3. Results

Figure 2 shows normalized curves of the studied structure magneto-optical rotation. They have a step-like behavior. First, in a relatively small magnetic field (< 250 Oe) the free iron layer is re-magnetized, then, in the field (500–1200 Oe) the fixed layer is switched. It is seen that Fe switching field decreases as the temperature grows. This can be explained by the fact that inter-layer exchange interaction between the free and fixed layers also depends on the temperature and is characterized by magnetic properties of FeAl interlayer, namely, correlation length of the exchange interaction. We are interested in the range of magnetic fields where re-magnetization of the free layer (Figure 1, *b*) occurs, since

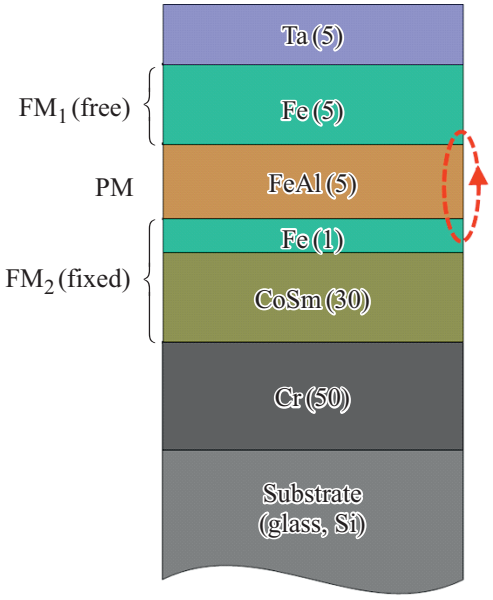

Figure 1. Scheme of the studied structure.

the process of magnetization redistribution in the interlayer takes place because of the redistribution of the magnetizing efficient exchange field, and, hence — change of magnetic entropy in it [4–6]. Using Maxwell relationship, from the plotted magnetooptical curves we may approximately calculate the entropy change ΔS_v of FeAl unit volume, integrating the difference of the structure magnetizations under various temperatures across the magnetic field in the range where free layer switching occurs

$$\Delta S_v \approx \frac{h_1}{h_s} \int_{H_{\uparrow\uparrow}}^{H_{\uparrow\downarrow}} \left(\frac{[M(T_i - M(T_{i+1}))]}{T_i - T_{i+1}} \right) dH, \qquad (2)$$

where h_1 — thickness of free layer, h_s — interlayer thickness, $i = 1, 2, 3, 4$ and T_i — temperatures from $T_1 = 398$ to $T_5 = 295$ K. At each temperature interval $T_i - T_{i+1}$ the obtained value $\Delta S_v(T_i)$ was assigned to the average temperature value in this interval, $(T_i + T_{i+1})/2$.

It was assumed in the calculation that magnetization of the fixed layer in the integration range remains unchanged. The magnetization of Fe free layer was taken from the measurement of ferromagnetic resonance of equivalent iron films grown in the same vessel and in the same process conditions and was equal 1400 G. The limits of integration $H_{\uparrow\uparrow}$ and $H_{\uparrow\downarrow}$ for magnetic field corresponded to the magnetization curves inflection points for the structure free layer. The magnetocaloric efficiency was defined as a ratio of magnetocaloric potential $\Delta S_v(T_i)$ to the range of magnetic fields $\Delta H = H_{\uparrow\uparrow} - H_{\uparrow\downarrow}$ in which it was calculated. Figure 3 illustrates the obtained temperature dependence of the magnetocaloric potential ΔS_v and magnetocaloric efficiency $\Delta S_v/\Delta H$ of the studied structure.

Maximal value $\Delta S_v/\Delta H$ was observed at a temperature of 385 K and made $2.05 \cdot 10^4$ erg/cm$^3 \cdot$ K $\cdot$ Oe. This value is

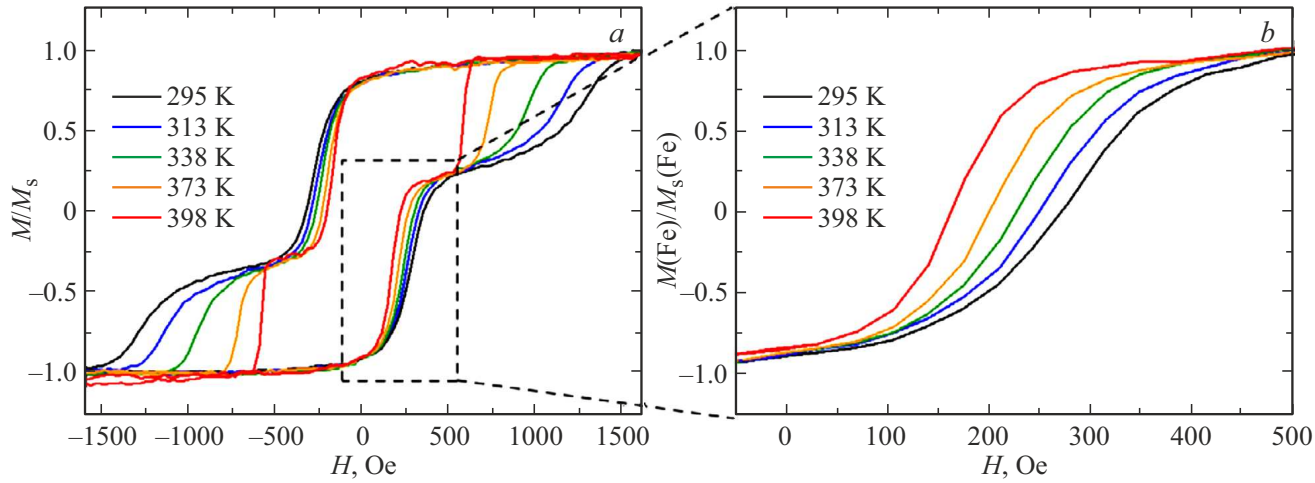

Figure 2. Normalized curves of the studied structure magneto-optical rotation.

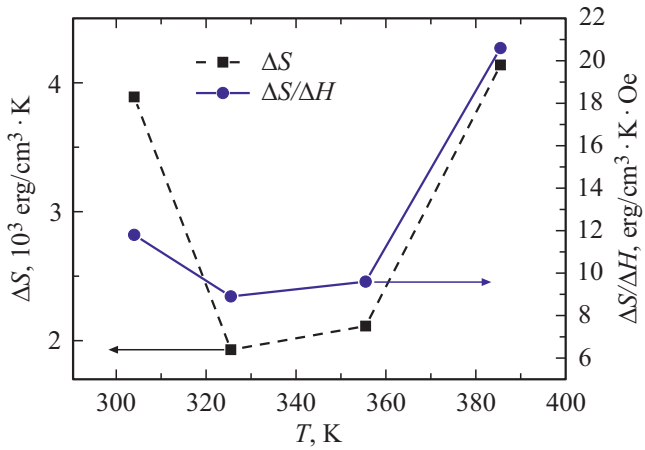

Figure 3. Temperature dependence of the magnetocaloric potential ΔS_v and magnetocaloric efficiency $\Delta S_v/\Delta H$.

comparable with magnetocaloric efficiency of Gd interlayer which is 3 nm thick as described in paper [7].

It shall be emphasized that not only switching field, but the re-magnetization curves slope of both, the free and fixed layers, depend on the temperature which may be associated with heterogeneity of inter-layer of exchange interaction of the sample area. The heterogeneity of inter-layer exchange interaction, in its turn, is caused by partial ordering of FeAl alloy right after the structure sputtering, i. e. availability of areas in FeAl layer that have superstructure which is proved by the study of electronic micro-diffraction.

To study the structure by method of transmission electron microscopy a film of $Fe_{0.55}Al_{0.45}$ 20 nm thick was grown on a free-hanging Silicone nitride membrane (Tedpella). The study was carried out with LIBRA 200MC (Carl Zeiss, Jena) transmission electron microscope at an accelerating voltage of 200 kV fitted with a monochromator and Gatan Ultrascan 4k digital camera. The experimental data were processed in Gatan Microscopy Suite 3.5.0. The electron micro-diffraction on the sample is featuring a ring structure typical for the poly-crystals. The superstructure peaks in the section of the ring diffraction are designated by arrows (Figure 4).

The disordered BCC-structure of A2 type is featuring the diffraction ring extinction with indices (100). If an ordered BCC phase appears (B2 type of structure) this ring of small relative intensity occurs. The degree of ordering can be defined by comparing with the known diffraction data for the following ratio:

$$S = \frac{\sqrt{I_{100}^{\exp}/I_{200}^{\exp}}}{\sqrt{I_{100}^{pdf}/I_{200}^{pdf}}},$$

where $I_{100}^{\exp}$ and $I_{200}^{\exp}$ — respective experimentally measured intensities of diffraction rings with corresponding indices, and $I_{100}^{pdf} = 8\%$ and $I_{200}^{pdf} = 14\%$ — intensity of diffraction rings known from the crystallographic database of powder diffraction (see card PDF 00-033-0020). The measured intensity values were $I_{100}^{\exp} = 302$ and $I_{200}^{\exp} = 382.1$, which gives the ordering parameter $S = 0.37 \pm 0.05$. After annealing at a temperature of 400°C for 2 hours this value increases up to $S = 0.75 \pm 0.05$.

Thus, because both, the ordered and disordered phases simultaneously exist in FeAl interlayer, its magnetic phase transition can be expected to have a broad range of temperatures. This can be explained by the absence of a distinct temperature dependence of the magnetocaloric potential and magnetocaloric efficiency. Moreover, as it has been mentioned before, a partial ordering of the interlayer effects the re-magnetization front width of the free and fixed layers. The heterogeneity of FeAl layer magnetic properties result in the heterogeneity of effective field of the interlayer exchange interaction across the structure area. With the sample temperature lowering together with the growth of effective field its scatter also grows which cases broadening of the magnetization curve. Thus, the range of

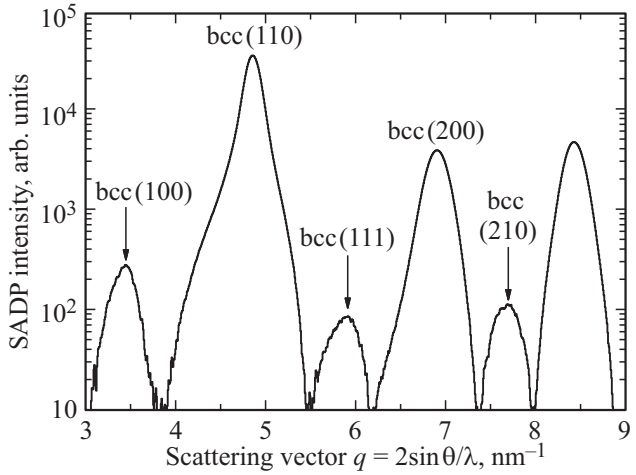

Figure 4. Cross-section of ring diffraction film of FeAl.

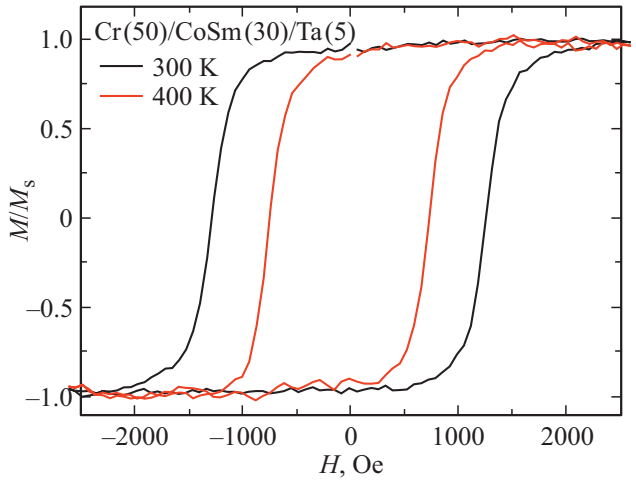

Figure 5. CoSm layer magneto-optical rotation curve.

the free layer re-magnetization field has increased from 200 to 350 Oe with the temperature change by 80°C, and for the fixed layer — from 100 to 450 Oe. Figure 5 shows the curves of magneto-optical rotation of CoSm layer in Cr(50)/CoSm(30)/Ta(5) structure for comparison.

As with the multi-layer structure the coercivity of CoSm insulated layer decreases with the temperature rise, however, the re-magnetization front width remains practically unchanged while in the multi-layer structure it changes in more than 4 times. This proves the suggestion that the magnetization curve broadening results from the heterogeneity of the inter-layer exchange interaction across the structure area. The broadening of magnetic fields range where the free layer is re-magnetized leads to lower magnetocaloric efficiency. This problem could have been solved by using homogeneous ordered FeAl inter-layer, however, to form the superstructure the annealing is required at a temperature of about400°C that will lead to partial mixing of FeAl inter-layer and adjacent layers of Fe.

4. Conclusion

An experiment was carried out to study the magnetocaloric properties of a thin FeAl(5) interlayer between strong Fe ferromagnets as a part of the multi-layered nanostructure Cr(50)/CoSm(30)/Fe(1)/$Fe_{55}Al_{45}$(5)/Fe(5)/Ta(5). Maximal value of the magnetocaloric efficiency obtained from measurements of the magnetooptical rotation curves with the use of Maxwell ratio was $2.05 \cdot 10^4$ erg/cm$^3 \cdot$ K $\cdot$ Oe, which is close to the value obtained for the thin Gd inter-layer [7]. The temperature dependence of the re-magnetization front width for the free and fixed layers of the structure resulting from the inhomogeneity of layers exchange interaction is caused by partial ordering of FeAl inter-layer which is proved by the electron microscopy studies. The studies show the possibility of FeAl use for creation of the 3D samples of composite magnetocaloric materials FM/PM with the effect of magnetocaloric potential exchange enhancement.

Funding

This study was supported financially by the Russian Science Foundation (project No. 23-22-00044).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Magnetic therapy of malignant tumors. Patent RF № 2295933.2007 Byull. No. 9. (in Russian).
[2] A.M. Tishin, Y.I. Spichkin. The magnetocaloric effect and its application.IOP Publishing Ltd., Bristol and Philadelphia (2003). 475 p.
[3] K.A. GschneidnerJr, V.K. Pecharsky, A.O. Tsokol. Rep. Prog. Phys. **68**, 1479 (2005).
[4] T. Mukherjee, S. Sahoo, R. Skomski, D.J. Sellmyer, Ch. Binek. Phys. Rev. B **79**, 144406 (2009).
[5] M.R. Dudek, K.K. Dudek, W. Wolak, K.W. Wojciechowski, J.N. Grima. Sci. Rep. **9**, 17607 (2019).
[6] A.A. Fraerman, I.A. Shereshevsky. Pis'ma v ZhETF **101**, *9–10*, 693 (2015). (in Russian).
[7] A.A. Fraerman. Pis'ma v ZhETF **113**, *5*, 353 (2021). (in Russian).
[8] M.A. Kuznetsov, A.B. Drovosekov, A.A. Fraerman. ZhETF **159**, *1*, 95 (2021). (in Russian).
[9] I.Y. Pashenkin, N.I. Polushkin, M.V. Sapozhnikov, E.S. Demidov, E.A. Kravtsov, A.A. Fraerman. FTT **64**, 10 (2022). (in Russian).
[10] R. Bali, S. Wintz, F. Meutzner, R. Hübner, R. Boucher, A.A. Ünal, S. Valencia, A. Neudert, K. Potzger, J. Bauch, F. Kronast, S. Facsko, J. Lindner, J. Fassbender. NanoLett. **14**, *2*, (2014).
[11] J. Fassbender, M.O. Liedke, T. Strache, W. Möller, E. Menéndez, J. Sort, K.V. Rao, S.C. Deevi, J. Nogués. Phys. Rev. B **77**, 174430 (2008).

Translated by T.Zorina