Magnetocaloric effect in multilayers studied by membrane-based calorimetry

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Abstract

We study magnetic multilayers, incorporating dilute ferromagnetic spacers between strongly-ferromagnetic layers exhibiting a proximity-enhanced magnetocaloric effect (MCE). Using magnetometry and direct measurements of the adiabatic temperature change based on a nanomembrane-calorimetry, we find that the MCE in the studied multilayer is indeed enhanced compared to that in the bulk spacer material. We develop a phenomenological numerical model of the studied trilayer and find that a long-range exchange interaction through the weakly-ferromagnetic spacer is required to adequately describe the magnetic and magnetocaloric properties of the system.

Keywords: adiabatic temperature change, thin film, magnetic multilayers, magnetocaloric effect, magnetic nanostructures, long-range exchange interaction, calorimetry

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of the giant magnetocaloric effect (MCE) in Gd₅(Si₂Ge₂) [1], the literature reveals a steadily growing interest in the area of MCE and magnetic cooling, in particular. The related technology of adiabatic demagnetization refrigeration (ADR) is expected to benefit from the new materials and offer cheaper, robust, more compact, and long-lasting solutions than the commonly used gas-based heat pumps, with the ultimate goal of reducing energy loss and the greenhouse gas emissions [2–6]. Even though some of the currently available MCE materials can be relatively eco-friendly in the long run, they often need expensive, difficult-to-mine rare-earth elements, which can neutralize their benefits when compared to the gas-based systems.

The majority of the MCE-related literature is on developing new complex alloys and compounds in the bulk form; only a small fraction of the MCE-related articles are on MCE in films, multilayers, and other low-dimensional structures [7]. In contrast to bulk materials, nanostructures exhibit finite-size effects (due to surfaces and interfaces), which can significantly alter their MCE with respect to that intrinsic to the incorporated materials [8–13]. This can yield novel properties and offer benefits that are unavailable with bulk MCE materials. For example, for a spin valve-like structure with a weakly ferromagnetic spacer [14–16], magnetic fields as small as a hundred oersted could be enough to induce significant MCE [17] due to the magnetic proximity effect (direct interlayer exchange across the interfaces). Recent works [18–21] have investigated such multilayered structures using magnetometry and concluded that the MCE is indeed enhanced, however, no direct magnetocaloric measurements are available. In spin valve-type structures with indirect interlayer exchange (RKKY), arranged such that its constructive versus destructive interference (on parallel to antiparallel switching of the spin-valve’s magnetization) yields a change in the
effective field acting on the dilute ferromagnetic spacer layer of the order of hundreds of kOe [22]. Such a field is strong enough to de/magnetize the spacer layer and induce a giant MCE. Another mechanism for enhancing MCE was demonstrated [12] using CoFe2O4/La0.1Sr0.3MnO3 heterostructures and relies on the interfacial strain-induced magnetostructural coupling in the system. The possibility of tuning between positive and negative MCE in Co/Cr superlattices has been reported [10]. The above-mentioned results illustrate how an enhanced MCE can be obtained from tailoring the interlayer interactions in a nanostructure, rather than by changing the intrinsic properties of the constituent materials. Often, the task is reduced to enhancing the effective de/magnetization field via interfacial spin–spin or spin–orbit interactions and focusing on the MCE-active region of the nanostructure, designed to have high magnetic susceptibility.

One of the promising nanostructured materials expected to have enhanced MCE is a trilayer of two strongly ferromagnetic films separated by a thin weakly ferromagnetic spacer, F/F/f/F [14–17]. Here, F, p, and F denote a pinned and a free strongly ferromagnetic layers, respectively, with their Curie temperature much higher than the operating temperature range of the MCE material. f is a weakly ferromagnetic spacer with Curie temperature (Tc) much lower than that of the F-layers. It is typically a transition metal alloy, designed to have a Curie temperature in the desired operating range by tailoring the magnetic dilution of the alloy. The pinning of the Fp layer can be achieved by exchange bias, high intrinsic anisotropy, or any other effect that is capable of strongly pinning the magnetization of the layer. Exchange-enhanced MCE in this design is due to the interplay of the magnetic proximity effects from the two F/f interfaces within the nearly paramagnetic spacer when the F-layers are switched between the parallel (P) and antiparallel (AP) magnetization orientations. Such magnetic multilayer systems were investigated previously in view of the influence of the proximity effect on, e.g. the induced magnetic properties of a Pt spacer [23] and the transport properties of a dilute magnetic semiconductor [24].

Previous work [18–21] on experimentally determining the magnitude of the MCE in the Fp/f/f/F system was conducted using an indirect method relying on macroscopic magnetization measurements, with the assumption that the analysis of the M–H curves based on the Maxwell relation applies to the orientational transition of the strongly ferromagnetic outer layers (P-to-AP), namely, that the P–AP switching is affected by the state of the spacer (f). The model took the magnetization throughout all layers to be along one axis (z-axis, collinear with P/AP magnetization states) as well as only nearest neighbor interatomic exchange in the paramagnetic spacer. Others [25–27] have modeled the system and obtained a twisted spin state in the spacer in the AP configuration, similar to a domain wall, highly sensitive to temperature due to the low Curie point of f. Additionally, it was shown [28] that a more accurate description of the switching behavior in a metallic F/f/f/F trilayer requires a long-range interaction term in the total energy of the system, especially within the dilute ferromagnetic spacer.

The applicability of the thermodynamic Maxwell relation to modeling the magnetization reversal loops of a system of type Fp/f/f/F must be carefully examined as M–H loops obtained using regular magnetometry (such as VSM) represent an orientational change of the field-projection of the total magnetization dominated by the F-layers, whereas the MCE is related to the changes in the magnetization of the spacer, which are most often indistinguishable by magnetometry. Compounding the difficulties with the Maxwell-relation approach, the presence of typically significant anisotropy and coercivity in the magnetization reversal behavior of the strongly ferromagnetic layers must be carefully analyzed and understood as their contribution to the overall M–H response of the system can be predominant. These considerations make the indirect (via magnetometry) methods of evaluating the MCE in the discussed F/f/F system uncertain and prompted us to implement a nanomembrane-based measurement technique for directly measuring the adiabatic temperature change of the multilayer material undergoing P–AP magnetization reversal in an applied magnetic field.

2. Samples and methods

2.1. Magnetic multilayers

The multilayer samples under investigation were fabricated using magnetron sputtering from multiple targets in a UHV chamber (ATC Orion system by AJA Inc.). The base pressure in the chamber was lower than 1E–8 Torr. The Ar pressure during the deposition was 3E–3 Torr. The deposition rates of Py (Fe20Ni80), Fe, FeMn (Fe50Mn50), and Cr were calculated from a nanoprobe-based calibration of the thickness of the films deposited for each target separately. The Fe,Cr100−x (x = 30) alloy was deposited by co-sputtering of the Fe and Cr targets. The atomic ratio x in the Fe,Cr100−x alloy was controlled by the ratio of the deposition rates of Fe and Cr. The obtained thickness of the deposited stacks was in good agreement with the calculated one. To select a direction for the exchange bias of the pinned layer, a DC magnetic field of 400 Oe was applied to the substrate during the deposition process. During the film growth, to achieve a more uniform deposition, the substrate (with DC magnets) was rotated with a frequency of 32 rpm.

The spacer was chosen to be FeCr because of a straightforward correlation of the proportion of Fe in Cr with the Curie temperature of the alloy. The value of the MCE in bulk Fe30Cr70 is relatively low (<0.1 J kg−1 K for field change 0–1 kOe) [29], nevertheless, it was found to be sufficient in strength and optimal methodologically to act as a calibration for the direct MCE-measurement technique used.

The deposited Fp/f/F multilayers have a well-known structure of a spin valve. In a conventional spin valve, the spacer between the pinned and free layers is nonmagnetic, whereas in the system under investigation the spacer is a dilute ferromagnetic alloy with the bulk Curie temperature designed to be close to 160 K. The schematic of the stack is shown in figure 1. To provide better adhesion and improve the growth
To detect the adiabatic temperature change of the magnetic multilayer a micro-sensor was fabricated consisting of a 50 nm thick Ti–O planar thermistor with high temperature coefficient of resistance (TCR = 1%–3%) deposited on a 100 nm SiN membrane (Silson Ltd UK). The thermistors were deposited using reactive magnetron sputtering from a Ti target in a mixed atmosphere of Ar and O₂. The thickness control of the Ti and SiO₂ was done in the same way as for the magnetic multilayer. To electrically isolate the thermistor from the conductive magnetic film, a 15 nm layer of SiO₂ was deposited on top of the Ti–O layer. The key properties of nm-thin SiN membranes are their low heat conductivity and heat capacity, which make the MCE measurement conditions close to adiabatic [31, 32]. The micrograph and schematic of the membrane with the thermistor and the magnetic multilayer are shown in figure 2.

2.3. VSM measurements

The VSM measurements were carried out using a Lake Shore 7300 vibrating sample magnetometer equipped with a nitrogen gas-flow cryostat. The isothermal magnetization reversal loops were measured with the field applied in the plane of the films, with the exchange bias direction oriented along the positive direction of the field. The measured magnetization was normalized by the magnetic volume of the samples.

2.4. Membrane-based calorimetry

The schematic of the measurement setup is shown in figure 3. \( R_\text{x} \) denotes the Ti–O planar thermistor, deposited directly onto the SiN membrane, as the substrate for deposition of the magnetic multilayer to be studied. DC voltage \( U_\text{drive} \) is applied to voltage divider \( R_\text{g}–R_\text{x} \), where \( R_\text{g} \) is a current limiting resistor. The voltage drop across \( R_\text{x} \) is fed into a lock-in amplifier (LA). The membrane with the sensor and magnetic stack is placed in a vacuum inside a cryostat (Oxford OptistatDN, modified to operate without gas in the sample space to prevent parasitic sample-gas-chamber heat exchange). The cryostat is placed inside an electromagnet (M), which is powered by a power supply unit (PSU) capable of supplying an AC + DC current (Kepco BOP).

When a low frequency (11.7 Hz) AC magnetic field is applied to the magnetic sample, sufficient to induce MCE (strong enough to produce P–AP switching in spin-valve samples), the temperature of the sample placed in direct contact with the sensor/membrane changes synchronously with the external field. Due to the low heat conductivity of the membrane, a momentary change in its temperature equilibrates over a relatively long period of time, \( \tau > 0.1 \) s in our case (time constant of our membrane sensor). Thus, for the applied field frequency that exceeds \( 1/\tau \) the condition for the temperature change of the sample to be adiabatic is fulfilled (it changes/oscillates faster than it can dissipate to the bigger substrate via the membrane). The magnetic sample is in direct contact with the thermistor, whose resistance \( R_\text{x} \) oscillates producing a variation conditions a 5 nm Cr seed layer was used. Also, a 5 nm Cr layer was used to protect the top of the multilayered film. For a higher signal-to-noise ratio in both vibrating sample magnetometry (VSM) and direct MCE measurements, the Py/Fe₃₀Cr₇₀/Py/FeMn/Cr structure was sequentially deposited three times and the Cr layers served as magnetic isolation between the top FeMn layer and the bottom free Permalloy layer of the next stack.

For this study, we deposited six samples, three of which onto thermally oxidized Si substrates (‘s’ series) and three onto home-fabricated sensors based on 100 nm SiN thin membranes for direct MCE measurements (‘m’ series). The naming and description of the samples are shown in table 1.

The magnetic properties of the multilayers deposited onto oxidized Si substrates should essentially be the same as those deposited on the membrane sensors, which are capped with a 15 nm thick insulating layer of SiO₂ (sensor details below). To verify this, two identical magnetic stacks were deposited onto a bare oxidized-Si substrate and onto a Ti–O layer (sensor material) prepared on the same substrate, where the Ti–O was capped with 15 nm of SiO₂. VSM \( M–H \) measurements for the two samples showed only minor differences in the behavior of the magnetization and, therefore, justified a comparative analysis of magnetometry-vs-MCE presented below.

Samples sA and mA were the focus of the study, expected to show an enhanced MCE compared to that in sample mC with the reference value of MCE of the bulk spacer material. The thickness of the Fe₃₀Cr₇₀ alloy film in samples sC and mC was 50 nm and the \( T_\text{C} \) close to that of the bulk material [30]. We, therefore, in what follows refer to samples sC and mC as bulk samples.

Samples sB and mB have the same structure as sA and mA but a nonmagnetic spacer, which at 6 nm thickness should not mediate any significant magnetic exchange (direct or indirect) between the free and pinned strongly ferromagnetic layers. This sample is used as an additional control sample in the direct measurements of the adiabatic temperature change of the multilayers, as it should not show any signal related to the MCE in the spacer (Cr spacer is non-magnetic), while it should reveal any spurious contributions that may be present in a membrane-based MCE measurement.

| Table 1. Multilayer composition and sample notations. |
|------------------|------------------|------------------|
| Si/SiO substrate | SiN membrane     | Deposured structure |
| sA               | mA               | Cr/Py/Fe₃₀Cr₇₀/Py/FeMn/Cr |
| sB               | mB               | Cr/Py/Py/FeMn/Cr |
| sC               | mC               | Cr/Fe₃₀Cr₇₀/Cr |

Figure 1. Schematic of Py/Fe₃₀Cr₇₀…/Py/FeMn stack.
we have and the vectors measured by lock-in signals as MCE signal as tor of the parasitic inductive pick-up as of the AC magnetic field, the inductive pick-up is detected sensor—the one used in this article. 

As the MCE-related signal is detected at the first harmonic of the AC magnetic field, the inductive pick-up is detected with the phasor approach to signal processing. Two measurements are carried out consecutively, with positive and negative DC field offset and the properties of the magnetic system, the MCE signal can be detected at the first or the second harmonic. In what follows, we limit the discussion to the most straightforward case of a low-amplitude AC field applied at various fixed biasing fields, such that the signal is found predominantly at the 1st harmonic (details below).

The size of the planar thermistor must fulfill two main criteria: the volume of the active MCE material must be relatively large to provide a significant change in temperature of the membrane/sensor/trilayer stack; the sensor/trilayer must be relatively small to avoid the unwanted heat exchange with the bulk Si substrate. We have modeled these aspects numerically for a given membrane geometry, AC-field frequency, and material parameters, and arrived at the optimal size of the sensor—the one used in this article. As the MCE-related signal is detected at the first harmonic of the AC magnetic field, the inductive pick-up is detected together with the MCE signal. It is unwanted and is removed using the phasor approach to signal processing. Two measurements are carried out consecutively, with positive and negative $U_{\text{drive}}$ applied to the $R_b$--$R_s$ voltage divider. Denoting the vector of the parasitic inductive pick-up as $\mathbf{P}$, the vectors of the MCE signal as $\mathbf{S}_1$ and $\mathbf{S}_2$ (for positive and negative $U_{\text{drive}}$), and the vectors measured by lock-in signals as $\mathbf{L}_1$ and $\mathbf{L}_2$, we have

$$\begin{align*}
S_1 &= -S_2 = S_{\text{MCE}} \\
P + S_1 &= L_1 \\
P + S_2 &= L_2
\end{align*}$$

With vectors in polar coordinates

$$\mathbf{L}_a = (R_i, \theta_i), \quad S_{\text{MCE}} = (S_{\text{MCE}}, \theta_{\text{MCE}}),$$

the system (1) gives us

$$S_{\text{MCE}} = |S_1| = \frac{1}{2} \sqrt{R_1^2 + R_2^2 - 2R_1R_2 \cos(\theta_1 - \theta_2)},$$

$$\theta_{\text{MCE}} = \tan^{-1} \frac{R_1 \cos \theta_1 - R_2 \cos \theta_2, R_1 \sin \theta_1 - R_2 \sin \theta_2}.\tag{3}$$

The AC component of the resistance of the sensor ($R_{\text{AC}}$) is equal to

$$R_{\text{AC}} = \frac{(R_{\text{DC}}R_1 + R_0[R_{\text{DC}} + R_1])^2 S_{\text{MCE}}}{-R_{\text{DC}}R_1^2 U_{\text{drive}} + (R_0 + R_1) (R_{\text{DC}}R_1 + R_0[R_{\text{DC}} + R_1]) S_{\text{MCE}}}.\tag{4}$$

Here, $R_{\text{DC}}$ and $R_1$ are the DC resistance of the sensor at a given temperature. The input impedance of the lock-in amplifier (or preamplifier, if used).

For small changes in the thermistor resistance due to the AC-field induced MCE (our case), the temperature coefficient of resistance ($k_{\text{TCE}}$) of the sensor at a given temperature can be considered constant, hence the adiabatic temperature change becomes

$$\Delta T_{\text{ad}} = \frac{-R_{\text{AC}}100\%}{k_{\text{TCE}}R_{\text{DC}}}.\tag{5}$$

The heat capacity of the active MCE material is often comparable to or less than that of the sensor-membrane material, a scaling coefficient for $\Delta T_{\text{ad}}$ needs to be introduced to reflect the ratio of the MCE-active thermal mass to the total thermal mass of the device. Straightforward general considerations show that this thermal-mass correction coefficient, $k_A$, and the resulting $\Delta T_{\text{ad}}$ of only the MCE-active volume, should be
than a combined property skewed by the unimportant details, show the characteristics of the studied magnetic material rather than a combined property skewed by the unimportant details of the measurement device (its ‘dead’ thermal mass with heat capacity noted as $C_{\text{dead-mass}}$).

Changes in the heat capacity near the critical point ($T_C$ of FeCr), induced by the P-to-AP switching, can cause changes in the ratio $k_A$. Using the heat capacity data from [33] and the magnetization versus temperature data from [29] (bulk, in 1 kOe), we can obtain the upper bound on such changes in our system. The change in the spacer’s magnetization (MCE active material) upon switching P-to-AP is less than $2\%$, as revealed by the simulations presented in section 4.1. At the temperature of maximum MCE (174 K) the $2\%$ change in the magnetization corresponds to temperature change of roughly 2 K. For heat capacity, the corresponding change at 174 K is $(2 \text{ K}) \times (9.3 \text{ J K}^{-1} \text{ m}^{-3})$, or 0.6%. With $C_{\text{tot}} = C_{\text{dead-mass}} + C_{\text{MCE}}$, we have $C_{\text{MCE}} = C_{\text{dead-mass}}/(k_A - 1)$ and

$$\frac{k_A^{\text{new}} - k_A}{k_A} = \frac{\Delta C_{\text{MCE}}}{C_{\text{MCE}}} = 0.03\%.$$  

In other words, even with an overestimation of the heat capacity change in the active MCE material, the factor $k_A$ is virtually unchanged near the phase transition. Heat capacity of all other materials in the sensor device (membrane, thermistor, etc) are smooth functions of temperature around the magnetic transition.

3. Results

3.1. VSM measurements

Sample sB is a control sample, a spin valve with a nonmagnetic spacer, for which the magnetization reversal loops at $T = 180$ and $T = 290$ K are shown in figure 4(a). The behavior is classical behavior for a spin valve [34]—the hysteresis is composed of two characteristic minor loops. One of the minor loops has low coercivity and is centered at zero field, easily identifiable as switching of the free Py layer. The second minor loop has a higher coercivity and is offset in field, which corresponds to the exchange-biased transition of the FeMn-pinned Py layer. As expected, cooling from 290 to 180 K leaves the minor loop of the free Permalloy layer almost unchanged, while the offset of the pinned loop significantly increases due to a stronger exchange bias from the antiferromagnetic FeMn at low temperature. The amplitudes of the free and pinned layers’ minor loops have a ratio of 6:4, which corresponds to the thickness ratio of the respective layers.

The magnetic properties of the sA sample are similar to those observed in [14, 15, 18, 20]. The $M – H$ loops for three representative temperatures are shown in figure 4(b). At high temperatures, when the spacer is in its nominally paramagnetic state, the free and pinned layers are almost fully decoupled and their minor loops are detached from each other. Approaching the effective $T_C$ from above, the exchange coupling through the spacer increases, which mediates unidirectional anisotropy from the pinned layer and results in a visibly offset loop of the free layer (partially free at 210 K).

The temperature dependence of the bias field for the free and pinned layer loops for sample sA are shown in figure 5. The strength of the biasing field of the free layer, $H_{\text{bf}}^\text{VSM}$ and $H_{\text{bf}}^\text{MCE}$, increases from essentially zero at high temperatures to about 170 Oe at 130 K. The bias-field strength of the pinned layer, $H_{\text{bf}}^\text{VSM}$, shows an increase from room temperature (RT) down to about 210 K, after which it weakens on further lowering the temperature. This non-monotonic behavior is due to an interplay of two effects: first, the well-known increase and eventual saturation of the strength of the antiferromagnetic pinning at low temperature [35]; the second is related to a higher Zeeman torque, proportional to the effective thickness of the now strongly coupled Py layers at low-$T$, which counteracts the exchange bias and lowers the loop offset [35, 36]. The resulting functional form of $H_{\text{bf}}^\text{VSM}$ versus $T$ is non-monotonic, as shown in figure 5 (red curve).

From the low-temperature (150 K) magnetization reversal curve in figure 4(b) it may appear that the switching of the free layer is a viscous process accompanied by significant coercivity. This conclusion would however not be correct as the partial reversal of only the free layer’s magnetization plotted in figure 4(c) shows very low coercivity. The relatively high coercivity of the full $M – H$ loop in the field region of the switching of the free layer is due to the overlap of the narrow switching loop of the free layer and the wide switching loop of the pinned layer.

The partial magnetization reversal loops of the free layer at room temperature, figure 4(c), divides into three sections corresponding to the three repetitions of the multilayer. Sample sA with only one repetition was deposited for comparison, figure 4(c). The differences suggest that, in addition to the magnetic state/dilution of the spacer, the strength of the interlayer coupling depends on the roughness of the interfaces, which increases somewhat for thicker films. It is visible that for the second and third repetitions of the deposited spin-valve structure, the RT exchange bias of the free layer gradually increases (figure 4(c)).

3.2. Direct measurements of MCE

Using the membrane-based MCE device described above we have measured the magnitude of the temperature variation

$$k_A = \frac{C_{\text{tot}}}{C_{\text{MCE}}}, \quad \Delta T_{\text{ad}}^{\text{MCE}} = \Delta T_{\text{ad}}^{\text{measured}} k_A.$$  

(6)
caused by the AC modulation of the field applied to the sample. Typical 2D maps of the MCE signal versus peak-to-peak AC field and DC offset field for samples mA, mB, and mC are shown in figure 6.

The data for the 50 nm thick film of Fe$_{30}$Cr$_{70}$ alloy (mC sample) are shown in figures 6(a) and (b) for 150 and 295 K, respectively. At the high temperature, no signal is visible above the background noise. As the temperature is lowered, a clear signal appears and increases, reaching a maximum at $\sim$160 K. The typical appearance of the MCE signal shown in figure 6(a) remains the same at all temperatures where the signal is detected, changing only in intensity. The gap near zero DC field can be explained by the fact that at $|H_{DC}| < \frac{1}{2}H_{AC}^{pp}$, the value of the field-dependent entropy change $S(H_{DC} + \frac{1}{2}H_{AC}^{pp}) - S(H_{DC} - \frac{1}{2}H_{AC}^{pp})$ is lower than for the case of $|H_{DC}| > \frac{1}{2}H_{AC}^{pp}$, as $S(H)$ is an even function and becomes zero at $H_{DC} = 0$.

The sample with a spin-valve structure and a nonmagnetic spacer (mB) shows a relatively weak peak at 295 K (figure 6(d), marked with arrow), localized independently from the respective magnetization reversal loop in figure 4(a), for the same temperature. At lower temperatures, this peak broadens and shifts to a higher negative DC field (not shown), eventually (toward 170 K) moving out of the experimentally available field range (both AC and DC). This well-defined peak visible at 295 K is heating/cooling due to the reversal of the pinned Py layer, which is likely demagnetizing/frustrating a portion of the spins at the F/AF interface, some of which are uncompensated [37]. This MCE of the F/AF interface is outside the focus of the present study and will not be discussed further,
however, it is an interesting topic in itself and deserves a separate investigation.

A background signal linearly proportional to the strength of the AC field is detected at lower temperatures. It is DC-field unspecific and, therefore, does not complicate the interpretation of MCE peaks related to the F-layer magnetization switching, which is found at specific DC fields.

For sample mA, two well-distinguishable peaks are observed in the temperature range 150–290K. At room temperature, the first peak (marked with arrow 1 in figure 6(f)) is located near zero field and has a somewhat lower strength (less bright) than the second peak (arrow 2). Additionally, the signal for peak 1 appears and saturates at a lower AC modulation field than that for peak 2. At low temperatures,
both peaks shift to higher negative DC fields and increase in both magnitude and width. The data for \( T = 170 \) K corresponding to the maximum MCE we have observed is shown in figure 6(e). At temperatures lower than 170 K both signals undergo a rapid change, both in magnitude and shape—they merge and become hardly distinguishable.

We identify peaks 1 and 2 as corresponding to the P-to-AP and AP-to-P switching of the free and pinned layers in the sample (mA—trilayer with dilute ferromagnetic spacer). Peak 1 corresponds to the transition where the magnetization of the pinned layer stays unchanged while that of the free layer reverses. Peak 2, then, is where the switching occurs in the pinned layer while the free layer is fixed by the relatively high DC field offset. This interpretation is supported by the independently measured \( M - H \) switching fields (see magnetometry data above), and naturally explains why the AC field required to induce peak 2 is higher than that for peak 1—the width of the partial \( M - H \) loop of the pinned layer is much larger than that of the free layer.

It should be mentioned that peak 2 in figure 6(f) at high temperatures possibly contains two magnetocaloric contributions—one from the proximity-enhanced MCE in the spacer, described in the previous paragraph, and one from the MCE that can be related to the F/AF interface and is observed in figure 6(d). As the amplitude of the latter is much lower and is observed only at high temperatures, we can neglect its contribution to the most prominent MCE regime depicted in figure 6(e), clearly identifiable as due to the relatively narrow P-to-AP transition on switching of the free layer at about 50–100 Oe in DC offset. The offset field of the MCE signal, related to the F/AF interface, may be different for samples mA and mA as the effective thickness of the pinned ferromagnetic layer is increased for sample mA due to the proximity-induced magnetization in the spacer. This may be the reason why the F/AF interface signal appears at slightly higher fields for sample mA compared to that for sample mA.

The dependence of \( \Delta T_{ad} \) on \( H_{AC} \) for samples mA and mC at the temperature of the maximum MCE signal are shown in figure 7. Since the \( \Delta T_{ad} \) signal for sample mC is delocalized in DC offset, the profile presented in figure 7 for this sample is the average value of \( \Delta T_{ad} \) for \( |H_{DC}| > \frac{1}{2} H_{pp,AC} \). For sample mA, the data presented in figure 7 is the profile of the map in figure 6(e) corresponding to the center of peak 1. The dependence for sample mC is linear with a positive slope, precisely as expected for a bulk-like alloy. At the same time for sample mA, the behavior of \( \Delta T_{ad} \) vs AC-field is clearly nonlinear, with a region of rapid growth followed by saturation. We denote the value of \( \Delta T_{ad} \) at saturation for sample mA as \( \Delta T_{ad}^* \).

The temperature dependence of the bias field of the directly measured MCE in sample mA (figure 5—purple curve) and the bias field of the partial \( M - H \) loop of the free layer in sample sA measured by VSM (figure 5—blue curve) are essentially identical. This leads us to conclude that the strongest MCE in the F/H/F structure is manifest on switching of the free layer, producing the P-to-AP transition in the system, with the weakly ferromagnetic spacer more frustrated in terms of its spatial spin orientation (higher magnetic disorder/entropy) between the oppositely magnetized interfaces of the outer F-layers in the AP state.

Figure 8 shows the data for the adiabatic temperature change measured directly on the membrane-fabricated samples, as well as that reported in the literature for the same composition bulk-like Fe–Cr alloy and extracted from magnetometry using the Maxwell relation [29] at the temperature of maximum MCE near 160 K. For samples mA and mC, MCE maps similar to those shown in figure 6 were recorded for the temperature range of 130–295 K. Using the data in figure 4(a) of [29] for \( \Delta S \) for an 88 nm Fe\textsubscript{80}Cr\textsubscript{70} film, the value of \( \Delta S = 0.024 \) J kg K\textsuperscript{-1} is obtained for the field changing from 0 to 250 Oe. Assuming a constant value of the heat capacity, \( C = 462 \) J kg K\textsuperscript{-1}, the maximum adiabatic temperature change in this case of the bulk-like alloy is \( |\Delta T_{ad}| \approx 0.008 \) K at \( 160 \) K (brown dash-dotted line in figure 8). The value of the peak adiabatic temperature change we measure directly for the same alloy (our 50 nm thick film of Fe–Cr; sample mC) and the one from the literature obtained indirectly are in good agreement. The Curie temperature for the Fe\textsubscript{80}Cr\textsubscript{70} sample estimated using the Arrott plots for the VSM \( M - H \) data taken at different temperatures for sample sC, is close to 160 K, which is in good agreement with the position of the maximum entropy change in our direct measurement as well as the literature [29, 30].

The \( \Delta T_{ad} \) vs \( T \) dependence for sample mA (figure 8 blue circles) shows a wide asymmetric peak with a maximum at \( \sim 170 \) K which is \( \sim 10 \) K higher than the Curie temperature of the Fe\textsubscript{80}Cr\textsubscript{70} alloy. The maximum measured MCE in the spin valve with the dilute ferromagnetic spacer is \( \sim 2.5 \) greater than the intrinsic MCE of the spacer material (taken here for the same external AC field amplitude). Further, the respective half-widths of the MCE signal are \( \sim 50 \) K versus 25 K, which means...
that, overall, the relative cooling power (RCP) per unit volume is approximately five times higher for the F/F/F trilayer [38].

Even though, at room temperature, the 6 nm Fe\textsubscript{30}Cr\textsubscript{70} spacer is in a paramagnetic state and the coupling between the two outer F\textsubscript{p} and F layers should be weak-to-absent [15], both the exchange bias of the F layer (nominally free) and the MCE signal of the trilayer are nonzero. These observations are rather fascinating since the correlation length of the ferromagnetic order parameter is nominally less than 1 nm for Fe\textsubscript{30}Cr\textsubscript{70} (at RT), suggesting that the direct interatomic exchange should not be expected to provide the observed finite exchange coupling through the 6 nm thick spacer at a temperature that exceeds the spacer’s \( T_\text{C} \) by nearly a factor of two.

An important characteristic of the investigated effect conclusively following from the data of figure 7 is the saturation of the MCE signal with the applied AC field amplitude for sample mA. This means that the magnitude of the MCE predominantly depends on the mutual orientations of the outer strongly ferromagnetic layers and not on the strength of the applied magnetic field, as is the case for the bulk-like Fe–Cr alloy film with a linear MCE-vs-Field dependence.

4. Discussion

The switching of the free layer and the corresponding \( \Delta T_{\text{ad}} \) signal in the studied system (sA and mA samples) are characteristically offset in field even at room temperature, which indicates a non-zero interlayer exchange coupling through the spacer, nominally too thick to mediate direct exchange as the spacer should be in a paramagnetic state, much above its Curie point. The presence of such exchange coupling at temperatures much higher than \( T_\text{C} \) in similar F/F/F structures was observed by several groups previously [14, 15, 18, 23, 28]. It has been suggested [28] that a long-range magnetic interaction (much longer than the usual inter-atomic exchange length scale) should be added to the energetics of the system in order to properly account for the observed interlayer coupling between the outer ferromagnetic layers at high temperatures and for thick (vs atomic scale) spacers.

A possible origin of such long-range coupling through a metallic spacer is exchange mediated by the polarized conduction electrons [39, 40] that traverse the stack and can transfer spin over longer distances. The spin-flip length \( \langle s_d \rangle \) in magnetic metals, which is the key characteristic in this process, varies from a few to a few tens of nanometers [41]. It is then reasonable to expect that in the dilute ferromagnetic metal-alloy spacer electrons polarized by the strongly ferromagnetic outer layers can mediate a significant amount of angular momentum over distances much exceeding the atomic spacing. The thickness of the spacer in our case is 6 nm, so no significant direct spin-transfer between the F-layers due to the conduction electrons is expected (RKKY essentially vanishes beyond 3 nm of Cr [42–44]). Therefore, in the model below, which uses a long-range interaction term, we restrict the action to the spacer spins only (40 monolayers for a 6 nm thick spacer). The spins in the spacer are affected by this long-range exchange from both F and F\textsubscript{p} and, effectively, form a spin-chain mediating a relatively small but finite F–F exchange coupling over several nanometers, at temperatures much exceeding the intrinsic Curie point of the spacer alloy, where the material in its bulk form would be in a paramagnetic state.

The need for a long-range spin-spin interaction term in quantitative modeling of the studied system can be illustrated with the following simplified argument based on our MCE vs \( T \) data of figure 8. For the spacer in a paramagnetic state (at \( T > T_\text{C} \)), its magnetic moment would be

\[
\mathbf{M}_\text{sp}(z) = \chi \mathbf{H}_{\text{eff}}(z),
\]  

where \( \chi \) is the magnetic susceptibility of the spacer in a paramagnetic state and \( \mathbf{H}_{\text{eff}} \) is the effective field within the spacer, which depends on the \( z \) coordinate normal to the plane of the F\textsubscript{p}/F stack (figure 9):

\[
\mathbf{H}_{\text{eff}}(z) = \mathbf{H}_\text{ext}(z) + \mathbf{H}_\text{f}(z) + \mathbf{H}_\text{p}(z) + \mathbf{H}_\text{ed}(z, T) + \mathbf{H}_\text{pd}(z, T).
\]  

Here \( \mathbf{H}_\text{ext} \) is external magnetic field, \( \mathbf{H}_\text{f}(z) \) and \( \mathbf{H}_\text{p}(z) \) are long-range effective field terms for the F/F and F/F/F interfaces, respectively, \( \mathbf{H}_\text{ed}(z) \) and \( \mathbf{H}_\text{pd}(z) \) are short-range effective exchange fields (direct-exchange proximity effect), which generally depend on both the temperature and coordinate, for the respective interfaces. At a temperature much above \( T_\text{C} \), the magnetization induced in the paramagnetic spacer at its F/F interfaces by the direct exchange fields \( \mathbf{H}_\text{ed} \) is significant, however, the respective penetration depth (due to direct inter-atomic exchange) is much smaller than the total thickness of the spacer. As a result, the induced magnetization vanishes off the two interfaces toward the center of the spacer; their overlap is essentially zero and, therefore, the difference in magnetization between the parallel and antiparallel configurations of the F\textsubscript{p}/F/F system expected from the short-range, direct exchange
can be neglected. At temperatures comparable or lower than $T_C$, this short-range term does produce an overlap in magnetization (different for P and AP, so $\Delta M \neq 0$ on P-to-AP switching) and must be taken into the account. A schematic of the multilayer with the spatial profile of the above effective fields is shown in figure 9. For the sake of this illustrative argument, we take the long-range exchange field (mediated by polarized electrons) as temperature independent, as it is expected to vary much weaker vs $T$ than the direct-exchange term, scaled by roughly the Fermi vs the Curie temperature.

Spin polarization of the electrons decays exponentially off the F/f interfaces into the spacer over a characteristic spin-flip length, $l_{sf}$, so the spatial dependence of the respective effective magnetic fields, $H_{f}(z)$ and $H_{p}(z)$, has the form

$$H_{f}(z) = M_{f}J_{f}e^{-z/l_{sf}} \quad \text{and} \quad H_{p}(z) = M_{p}J_{p}e^{(z-t)/l_{sf}},$$

(10)

where $t$ is the thickness of the spacer, $J_{f}$ and $J_{p}$—properly normalized exchange constants between the pairs of materials F/f and F/p, $M_{f}$ and $M_{p}$—magnetization vectors of the free and pinned layers, respectively. In figure 9 the fields for the long-range exchange are shown out of proportion for visual clarity—estimated to be about two orders of magnitude smaller than the corresponding short-range exchange fields (2% range used in the numerical simulations below).

With the magnetization of the spacer denoted as $M_{sp}(z)$, the energy areal density is

$$\varepsilon(z) = M_{sp}(z)H_{eff}(z).$$

(11)

Using (8) and integrating (11) over $z$, the magnetic energy per volume of the spacer becomes

$$E = \chi \int_{0}^{z} H_{eff}(z) dz.$$  

(12)

The energy difference, $\Delta E$, between the P (↑↑) and AP (↑↓) states of the trilayer is then

$$\Delta E = \chi \left[ \int_{0}^{z} H_{eff^{↑↑}}(z) dz - \int_{0}^{z} H_{eff^{↑↓}}(z) dz \right].$$  

(13)

Taking $H_{DC}$ as the field offset and $H_{AC}$ as the width of the P–AP transition, the effective fields for the two states projected onto the P/AP axis ($x$) are

$$H_{eff^{↑↑}}(z) = H_{DC} + H_{AC} + M_{f}J_{f}e^{-z/l_{sf}} + M_{p}J_{p}e^{(z-t)/l_{sf}},$$

$$H_{eff^{↑↓}}(z) = H_{DC} - H_{AC} - M_{f}J_{f}e^{-z/l_{sf}} + M_{p}J_{p}e^{(z-t)/l_{sf}}.$$  

(14)

According to the Landau theory of phase transitions, above the Curie point, $\gamma \propto C(T-T_{C})^{-\gamma}$, where $\tau = T - T_{C}$ and $\gamma$ is the critical exponent for the Curie transition. With constant heat capacity $C$, this gives for the entropy change on P–AP switching versus temperature

$$\Delta S = \frac{\partial \Delta E}{\partial \tau} = -C \gamma \tau^{-(\gamma+1)} \int_{0}^{z} \left[ H_{eff^{↑↑}}(z)^{2} - H_{eff^{↑↓}}(z)^{2} \right] dz$$

(15)

or $\Delta S(T) \propto \tau^{-k}$, with $k = \gamma + 1$. Figure 10 shows $\Delta S$ converted from the experimentally measured $\Delta T_{ad}$ data of figure 8, alongside $C(T - T_{C})^{-k}$ fitting at high temperatures, with $T_{C} = 162$ K and $k = 2.28 \pm 0.25$ and $2.23 \pm 0.1$ for the mA and mC samples, respectively. The fitting yields the critical index, $\gamma$, close to 1.3 for both samples, which is rather interesting as this value is characteristic for paramagnetic $\chi(T)$ and, at first glance, not expected to apply to the F/F/F structure. The explanation of the high-temperature critical-exponent behavior discussed below sheds additional light on the MCE mechanism at play in the studied system.

For the bulk-like sample (mC), obviously, both short- and long-range effective exchange fields are absent as there are no interfaces, so only the external fields affect the material. In this case, at a given temperature (14) and (15) reduce to $\Delta S(H) \propto H_{DC}H_{AC}$. With $H_{DC} = \text{const}$, $\Delta T_{ad}$ (or, equivalently, $\Delta S(H)$) should be linearly proportional to $H_{AC}$, which is indeed observed experimentally; see figure 7, red triangles for sample mC.
In contrast, for the F/F/F trilayer, the P–AP switching of the magnetization results in a rather sharp, step-like behavior, with a characteristic saturation at a field where the magnetization of the free layer is fully rotated; figure 7, blue circles for sample mA. The effect is normalized to the volume of the MCE active layer (spacer or thick film), so that the fact that the initial $\Delta T_{ad}$ vs $H_{AC}$ of the trilayer is much steeper than that of the thick film indicates that the effective (exchange) field producing the response is much stronger than the externally applied field. Naturally, as the magnetization vector of the free layer rotates, its proximity field within the spacer (mostly long-range component at higher temperatures and mostly direct exchange near $T_C$) follows the rotation and partially cancels out that from the pinned layer when the rotation is complete (AP state). The resulting relatively large (as it is of exchange origin) effective-field differential as given by (15) is expected to scale with the angle of rotation, produce a steep slope, and saturate when in the AP state. This picture applies above as well as near the Curie point and describes well the experimentally observed behavior, shown in figure 7.

Interestingly, the fact that the 295 K data has the same functional form of step-saturation as the 170 K data (figure 7, green diamonds), justifies the assumption that a weakly temperature-dependent, long-range exchange is present in the structure at temperatures much higher than the transition point. Otherwise, with the direct-exchange proximity fields (very short-range at high-$T$) fast-decaying and not overlapping in this regime, the external field would be expected to produce a linear slope of the type seen in the mC sample data. In the Simulations section below, we will discuss in detail domain-wall-like spin distributions within the spacer in the AP state responsible for this MCE behavior and how they vary with temperature and exchange characteristics.

The above qualitative argument offers a compelling illustration of the mechanisms behind the studied phenomenon. However, the presence of the intrinsic interatomic exchange inside the spacer material, including the range above its Curie temperature, should be expected to contribute and likely modify, at least quantitatively and potentially significantly, the MCE in the F/F/F system near and below $T_C$. We, therefore, have conducted in-depth numerical simulations of the system in a wide parameter space, including direct-proximity as well as long-range exchange interactions. A computationally efficient phenomenological model was developed for large phase-space mapping of our system, which is difficult to do using other approaches, such as the well-established but more resource intensive atomistic spin dynamics. (The latter is discussed in detail elsewhere [45], showing good qualitative agreement with the conclusion herein in regions of overlapping parameter space, e.g. when only short-range exchange is present).

The results of the numerical simulations are presented below and show that the AP state of the trilayer near and above $T_C$ has a nontrivial spin configuration similar to a Bloch domain wall. It is this configuration left out by the paramagnetic-spacer model that actually determines the strength of the MCE in the system and its variation with temperature and composition.

### 4.1. Numerical simulations

Atomistic spin simulations of our system [45], which would incorporate long-range spin–spin interactions (the full width of the spacer of 6 nm, up to the 591st nearest neighbors), would be extremely time- and resource-consuming. We, therefore, develop here a phenomenological computational model [46], simulating the F/F/F system as a stack of magnetization vectors representing atomic monolayers throughout the trilayer. The magnitude of the magnetization of a monolayer is defined by the Brillouin function of temperature and the local effective field, consisting of a Zeeman term and the intra- and inter-monolayer exchange contributions. The strong out-of-plane demagnetization in our thin film geometry restricts the spins orientationally to the film plane. One of the ferromagnetic layers is ‘pinned’ by a fixed static field of 450 Oe, the other has no in-plane anisotropy and would be free to rotate in a variable external field in case the spacer was fully nonmagnetic.

The simulation algorithm consists of sequentially updating magnetization magnitudes and orientations using iterative processes, while continuously updating the effective fields, as shown by the following pseudo-code:

```pseudo-code
while n <= 90000 & cond_M & cond_phi
    for k = 1 .. 35
        find magnitude M_k from M_k-1
        update effective field H_eff
    end
    for f = 1 .. 100
        find angle phi_f from phi_f-1
        update effective field H_eff
    end
    n = n+1
end
```

The equation for updating the magnetization magnitude of a given monolayer, line 3 in the pseudo-code above, is

$$M^k = M_0 B (H_{eff}, T, M^{k-1})$$

(16)

where $M_0$ is the monolayer’s saturation magnetization at 0 K and $B$ the Brillouin function that has as the input the effective field, $H_{eff}$, the temperature, $T$, and the value of the monolayer’s magnetization from the previous k-iteration, $M^{k-1}$.

The equation for updating the effective field, line 4 and 8 in the pseudo-code, is

$$H_{eff} = H_{ext} + H_{ex}(\gamma_d, \gamma_l, \varphi_M, M^{n-1}_{m}, M^{n-1}_{l})$$

(17)

where $H_{ext}$ is the external magnetic field and $H_{ex}$ the exchange field. The latter depends on the magnetization of the nearest and next-nearest neighboring monolayers obtained in the previous n-iteration ($M^{n-1}_{m}$) as well as the magnetization of the monolayers within the range of the long-range interaction ($M^{n-1}_{l}$). $\gamma_d$ and $\gamma_l$ are pairwise exchange coefficients for direct and long-range exchange, respectively. $\varphi_M$ is the (updated, most recent) orientation of the magnetization vector of the monolayer addressed in the current iteration step.
Orientations $\varphi_M$, lines 6–9 in the pseudo-code, are updated using the gradient descent method, with the magnetization vector of the given monolayer taken to be oriented along the effective field acting on it, $\varphi_M = \varphi_{M0}$ (characteristic to mean-field formalisms, such as the one used herein).

Conditions cond_N and cond_xphi on line 1 in the pseudo-code are $M < 10^{-7}$ emu cm$^{-3}$ and $\Delta \varphi_M < 10^{-6}$ deg. The final state of the system for various parameter combinations showed only minor changes after about 90k n-iterations, which was taken to be the maximum simulation length, sufficient to achieve good accuracy. The length of the k-iteration chain is chosen to be 35 and the f-iteration 100, which again were selected to yield good overall accuracy (verified by running occasional longer control simulations).

The values of the saturation magnetization and Curie temperature used in the simulations were obtained from the literature [47]. The Curie temperature of the spacer was chosen to be 160 K as this value was observed on the experiment. The Curie temperature of the free and pinned ferromagnetic layers was chosen to be 2000 K to minimize the variation of the F-layers’ magnetization with temperature. This approximation speeds up the simulations and essentially limits the variable part of the system to only the spacer, as we specifically aim to investigate the effect of the properties of the spacer on the overall behavior of the trilayer. The strength of the intrinsic exchange in the spacer was chosen so as to reproduce the experimentally observed Curie temperature (160 K). The strength of the short-range proximity exchange between the FeCr and Py layers (at F/f interfaces) generally depends on the quality of the interfaces and, for our samples, was numerically estimated to be about 150% of the intrinsic exchange in the spacer. The set of parameters used in the simulations is shown in table 2.

To qualitatively reproduce the magneto-statics observed on the experiment, two simulations of the F/f/F system were performed using the aforementioned algorithm. We have compared the magnetostatic behavior of the system for the case where the only exchange interaction available is direct exchange with the nearest and the next nearest neighbors, and the case where the direct short-range exchange is supplemented by long-range exchange interactions between the interface spins of the F layers and the spins in all of the spacer (with spatially decaying strength). In what follows, we refer to these two types of simulations as ‘without long-range exchange’ and ‘with long-range exchange’. The long-range exchange constant is taken to have the same $\gamma$-dependence as the corresponding exchange field given by (10):

$$J_l(z) = J_{0f} e^{-z/l_d}, \quad J_p(z) = J_{0p} e^{(z-1)/l_d},$$

where $J_l(z)$ and $J_p(z)$ are the $\gamma$-dependent exchange constants proximity-induced within the spacer by the free and pinned F/f interfaces, $J_{0f}$ and $J_{0p}$—their interface values (at $z = 0$, the same as $\gamma$), $z$—the coordinate normal to the film plane, $l_d$—the characteristic decay length of the long-range exchange interaction (the spin-flip length in the spacer, assuming the effect is due to polarized electrons).

The simulated $M$–$H$ loops for the two model cases, namely, without and with the long-range exchange, are shown in figure 11. Parameters $l_d = 4$ nm and $J_{0f} = J_{0p} = 2\%$ of the intrinsic exchange in the spacer were found to optimally fit the measured data of figure 4. Although likely not the only one possible, this parameter combination is representative of the optimal range and is quite reasonable based on the general considerations of the energetics and the scale of spin relaxation and spin transfer in dilute ferromagnetic alloys.

It is clearly visible that with only the direct exchange, the coupling between the F and F layers through a 6 nm spacer fully vanishes at $T > T_C$, as the minor loops of the F layer are centered at zero field. In contrast, for the case with both the direct and long-range exchange, the inter-layer coupling survives up to room temperature, yielding a nonzero exchange bias of the free layer. This specific feature of the simulated magnetization reversal loop, which we find to be critically dependent on the presence of long-range exchange, reproduces the behavior observed experimentally in (figures 4(b)–(d)) and previously in [14, 15, 18, 23, 28].

A completed iteration sequence yields the equilibrium magnitude and orientation of the magnetization of each monolayer, for a given parameter set. As an example, the evolution of the simulated magnetization profile during the switching of the free layer, with the long-range exchange disabled and enabled, are shown in figure 12(a) and (b), respectively, for $T = 174$ K. Analyzing and comparing the data in figure 12(a) and (b), several important observations can be made. In the parallel state and with only short-range exchange enabled (point 1 in (a)), the proximity-induced magnetization decays exponentially from the F/f interfaces toward the center of the spacer, which in fact is expected for penetration of the magnetic order parameter in the Landau theory (for individual interfaces). Even though the direct exchange may induce substantial magnetization inside the spacer in the direct proximity of the F layers, this magnetization decays rapidly and vanishes toward the center of the spacer, and therefore can not provide either a significant change in magnetization on P-to-AP switching or any appreciable coupling between the outer F layers. With both direct and long-range exchange present (figure 12(b)), the P-state magnetization deviates from the above behavior and is an order of magnitude higher in the middle of the spacer compared to that for only direct exchange. A similar tendency is observed for the AP-state (point 2 in (a) and (b))—the magnetization profile functionally deviates from an exponential decay and this deviation is much stronger in the case where the long-range exchange is enabled. Due to a cancellation of the opposing effective exchange fields (AP-state), overlapping in the center of the spacer, the magnetization at $z = 7$ nm is drastically decreased, with the difference on

| Table 2. Exchange parameters used in simulations. |
|---|---|---|
| Material pair | $\gamma_d$ | $\gamma_l$ | Long range exchange length |
| Py–Py | 0.23 | 0 | — |
| FeCr–FeCr | 0.023 | 0 | — |
| Py–FeCr | 0.0345 | 0.0003 | Py—0.15 nm, FeCr—4nm |
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Figure 11. Magnetization reversal loops of $F_p/F$ system simulated to fit measured $M-H$ loops of figure 4: (a) without long-range exchange, i.e. with short-range exchange only; (b) with long-range exchange as well as short-range exchange.

Figure 12. Simulated magnetization magnitude and orientation through thickness ($z$) of $F_p/F$ system at $T=174$ K: (a) without and (b) with long-range exchange; $z = 0 \div 4$ nm is occupied by pinned layer, $4 \div 10$ nm—spacer, $10 \div 16$ nm—free layer. Solid lines indicate magnitude of magnetization vector (left axis) and dashed lines indicate its orientation (right axis). Insets: magnetization reversal loops with characteristic points indicated by numerals, $n=1, 2, 3$, where point $n$ corresponds to magnetization profile $M_n(z)$ and orientation profile $\theta_n(z)$.

P-to-AP switching being much bigger when the long-range exchange is present. The intermediate-state orientational profile (figure 12(b), point 3, dashed line for $\theta_3(z)$) reveals a scissor-like state in the system, with a $\sim 90^\circ$ ‘exchange spring’ in the spacer, which must be the reason for the absence of any significant cancellation of the effective exchange at $z = 7$ nm and hence no significant additional magnetic disorder. In contrast, the orientational transition is sharp in the AP-state ($\theta_2(z)$) with a well-defined 180-wall, a single nanometer in thickness, producing strong local magnetic disorder.

The switching of the free layer in the model with only direct exchange (inset to figure 12(a)) is step-like and no intermediate state is observed between the parallel and antiparallel configurations at all temperatures higher than the Curie temperature. Enabling long-range exchange results in non-vanishing interlayer coupling in a wide temperature range above $T_C$ and, consequently, in rotational states intermediate between P and AP. Due to this coupling, both magnetization vectors of the pinned and free layers tilt to an equilibrium orientation that is generally different from the direction of the external field (e.g. point 3 in the inset to figure 12(b)). The magnetization magnitude in the spacer decreases only slightly from its value in the P state for intermediate angles. Only in the vicinity of the AP state does the spacer demagnetize significantly in the very center, showing a narrow orientational spin transition similar to a Bloch domain wall.

The numerical simulations have a high illustrative and interpretational value as they yield the spatial spin profiles in the structure, which are difficult, if at all possible, to obtain on the experiment—VSM magnetometry yields only a projection of the net magnetic moment of the structure as a whole. Having the microscopic spin distribution sheds light on the mechanism behind the system’s magnetocaloric response and its strength. Thus, extracting the change in the magnetization magnitude on P-to-AP switching yields the change in magnetic disorder (or entropy of the magnon sub-system; between points 1 and 2 in the inset to figures 12(a) and (b)). This normalized magnetization difference is shown in figure 13, simulated with (blue) and without (green) long-range exchange. For comparison, the magnetization change in the bulk spacer material in response
to 250 Oe of the external field is shown in red. To convert the magnetization change to the magnetic entropy change, different approaches can be used, but the general relation is that $\Delta S \propto \Delta m$.

The key result presented in figure 13 is that for the trilayer system modeled with the long-range exchange enabled (blue) the strong magnetic disorder (MCE) induced by the P–AP transition persists to temperatures significantly higher than $T_m^s$, with the maximum $\Delta m$ shifted to slightly higher than $T_m^s$. This is in excellent agreement with the results of our direct MCE measurements shown in figures 8 and 10. At the same time, $\Delta m$ for the case of the trilayer with no long-range exchange as well as for the bulk system (simulated with direct exchange only) peak at $T_m^s$ and vanish directly above it. It is clear that the strength of the field-induced demagnetization is enhanced in the case of the F/f/F trilayer system, both with and without long-range exchange taken into account, compared to the case of the bulk alloy (thick film). Estimating potential MCE efficiency of the proximity-enhanced material versus that of the bulk spacer alloy, we note that the ratio of areas under $\Delta m$ of the respective materials is proportional to the ratio of their RCP [48]. This means that the RCP of the proximity-enhanced spacer (simulated with long-range exchange) can be up to two orders of magnitude higher than that of its constituent material. The simulated case with only direct exchange (green in figure 13) does show enhanced MCE and RCP, however, it clearly disagrees with the experiment as to the peak position and, especially, the high-temperature range where the effect is pronounced.

Comparing the simulated and the experimental results (figure 13 versus figure 10) we conclude that long-range exchange is necessary to adequately explain and quantify the observed MCE effect. The long-range exchange affects the magnetization profile within the spacer in a significant way, magnetizing the otherwise paramagnetic material into a domain-like spin distribution of spatially variable magnitude, which shows a strong change on P-to-AP switching in the structure, in a comparatively very low external field ($\sim 100$ Oe, $2 \div 3$ orders of magnitude lower than for conventional ADR systems). Long-range exchange is the key to having MCE peak noticeably above $T_m^s$ and extend in a strong fashion to temperatures significantly higher than $T_m^s$, which should be useful for extending the material’s operating range in device applications. Our experiment and simulations confirm that the concept of enhanced MCE in F/f/F systems is valid both in terms of higher peak entropy-change values as well as much higher RCP.

## 5. Conclusion

We have performed, using a membrane-based nanocalorimetry method, direct measurements of the adiabatic temperature change in magnetic multilayers designed for enhanced MCE. The measurements show that the volume and field normalized MCE induced by the magnetic proximity effect in a specially designed trilayer can be significantly higher than the conventional MCE in the corresponding bulk material. The respective RCP is vastly stronger, one to two orders of magnitude, due in particular to a much broader operating temperature range of the exchange-enhanced material. We, therefore, conclude that the approach of exchange-enhancing MCE in magnetic nanostructures is valid and effective in reducing the requirements on the externally applied magnetic field. The experimental MCE measurement technique was the key to these findings as the commonly used indirect magnetometry-based methods were found to be inaccurate when applied to the orientational magnetic transition in the studied multilayered system.

The obvious challenge with thin F/f/F type multilayered structures is the relatively small volume of the active material with enhanced MCE properties. This issue may be overcome by using spacer materials having intrinsically higher MCE as well as by vertical stacking of the core trilayer structure. The presence of the assisting F-layers roughly doubles the volume of the stack at no direct benefit to MCE. However, the fact that they can switch in low fields ($\sim 100$ Oe) at very high speed (sub-$\mu$s) makes feasible high-frequency cooling cycles, orders of magnitude faster than the typical paramagnetic ADR cycles where ramping up/down $\sim 50$ kOe field over minutes is required. Particularly attractive may be cooling of micro/nano-devices (compact sensors, sources, gates, etc) based on the very membrane platform we demonstrate, provided a mechanical arrangement for heat outflow can be integrated and synced with the AC field cycle.

We find that a long-range exchange interaction, alongside the direct exchange, must be taken into account in order to adequately describe the observed properties of the studied metallic trilayer system. This interaction can be due to the conduction electrons polarized by the strongly ferromagnetic outer layers, traversing the weakly ferromagnetic spacer, thereby mediating spin–spin exchange over...
several nanometers. Our phenomenological model, which includes such long-range exchange, has allowed efficient, wide parameter-space numerical simulations, which explain the experimentally observed behavior in an illustrative as well as quantitatively accurate way. The enhanced MCE effect is shown to be due to an exchange-spring in the spacer, pinched-off in the center on rotation into the antiparallel state of the device.

Data availability statement

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

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