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Magnetocaloric effect of thin Dy films

V.D. Mello[a], Ana L. Dantas[b,1], A.S. Carriço[c,*]

[a] Departamento de Física, Universidade do Estado do Rio Grande do Norte, 59600-900 Mossoró - RN, Brazil
[b] Department of Physics, University of Colorado at Colorado Springs, Colorado Springs, CO 80918, USA
[c] Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, 59078-970 Natal - RN, Brazil

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Abstract

We report a theoretical study of the magnetocaloric effect (MCE) of Dy thin films, and show that the confinement of spins in the direction perpendicular to the surfaces leads to a considerable enhancement of the MCE. The adiabatic temperature change, ΔT, for external field strength change, ΔH, of the order of a few kOe, is much larger than what is found in bulk Dy, reaching $\frac{\Delta T}{\Delta H} = 6$ K/T for ultra-thin films.

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In recent years a great deal of research effort has been dedicated to the investigation of the magnetocaloric effect (MCE).The motivation stems from the potential of solid magnetic systems for room temperature refrigeration,in substitution for traditional gas compression technologies. Magnetic refrigerators have higher thermal cycle efficiency and advantages concerning environmental safety [1,2].

MCE is characterized by a variation ΔT in the temperature of the magnetic material corresponding to an adiabatic change in the external magnetic field intensity. ΔT is a function of the initial temperature, T, and of the change in the strength of the external magnetic field, $\Delta H = H_f - H_i$. H_f and H_i are the final and initial values of the external field, and a positive MCE corresponds to having $\Delta T > 0$ for $\Delta H > 0$. Alternatively the MCE may be seen as the change in the magnetic entropy in an isothermal change of the external field intensity. Most commonly paramagnetic and ferromagnetic materials have positive MCE. In these materials an isothermal reduction of the external field produces a decrease in the splitting of the Zeeman levels, leading to a broader distribution of the population of the energy levels and an increase in the magnetic entropy. An interesting exception to this behavior has been recently reported for the paramagnetic material $PrNi_5$ [3]. In this material there is a crossing of the lowest energy levels, at low temperatures and large magnetic field strengths, leading to anomalous behavior of the magnetic entropy.

For ferromagnetic materials the reduction of the Zeeman energy splitting of the energy levels results from a combination of the direct effect of reducing the external field, and an indirect effect due to the reduction of the thermal value of the magnetic moment in the field direction. The internal fields, due to exchange energy, are extremely large at low temperatures, and the external field affects the magnetic order most significantly in the neighborhood of the Curie temperature. In the ordered phase ΔT is an increasing function of the temperature, with a maximum at the Curie temperature [1]. It has a "caret-like" shape whose width is inversely proportional to the temperature interval where order–disorder transition occurs. Helimagnetic materials have a rich phase diagram and a complex MCE. In the magnetic ordered temperature interval the external field may induce changes in the magnetic structure, without appreciable changes in the thermal average value of the magnetic moment per atom. The effect of external field on the magnetic entropy is dependent upon the field strength, and both positive and negative MCE may occur.

* Corresponding author. Tel.: +55 84 32153794; fax: +55 84 32153791.
E-mail address: acarrico@dfte.ufrn.br (A.S. Carriço).
[1] Permanent address: DCC, Universidade do Estado do Rio Grande do Norte, 59124-400 Natal - RN, Brazil.

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In order to qualify for magnetic refrigeration (MR) the magnetic material would ideally display both a large entropy change ΔS_M in an isothermal process, and a large temperature change ΔT in an adiabatic process, where the external magnetic field strength is changed. Both features affect the cooling capacity, q, which is given by:

$$q = -\int_{T_1}^{T_2} (\Delta S_M)\, \mathrm{d}T \tag{1}$$

and indicates the amount of heat that may be transferred from the cold end (at temperature T_1) to the hot end (at temperature T_2) of the refrigerator in one ideal thermodynamic cycle.

The isothermal change of magnetic entropy is given by:

$$\Delta S_M(T, H_i, H_f) = \int_{H_i}^{H_f} \left(\frac{\partial M(T, H)}{\partial T}\right)_H \mathrm{d}H, \tag{2}$$

and the adiabatic temperature change is given by:

$$\Delta T(T, H_i, H_f) = -\int_{H_i}^{H_f} \left(\frac{T}{C(T, H)}\right)_H \times \left(\frac{\partial M(T, H)}{\partial T}\right)_H \mathrm{d}H, \tag{3}$$

where $C(T, H)$ is the total specific heat, and includes both magnetic and elastic (lattice) contributions [1], and $(\partial M(T, H)/\partial T)_H$ is the temperature derivative of the magnetization at constant magnetic field. In the following we shall refer to processes with $H_i = 0$ and use $\Delta T(T, H)$ in the place of $\Delta T(T, 0, H)$, with $H = H_f$.

The MCE is to a large extent controlled by the value of $(\partial M(T, H)/\partial T)_H$. The heavy lanthanide metals are good materials for MR because they have large magnetic moments, with potentially large values of $(\partial M(T, H)/\partial T)_H$, and large molar magnetic entropy [2]. In the last two decades many new materials – including lanthanide materials, 3d material amorphous alloys, and manganites – with large MCE have been discovered, and a better understanding of the MCE phenomenon has resulted [4]. Gd and its alloys and compounds have been extensively studied [4–6]. Gd is the prototype material for room temperature MR, it has a Curie temperature around 293 K and a large MCE, with $\Delta T = 12$ K for an external field of 7 T, corresponding to $\Delta T(T, H)/\Delta H = 1.7$ K/T. For smaller field strengths the MCE is much larger, reaching a impressive field dependence of the MCE of 3 K/T [1].

In intermediate temperatures (80 K–180 K), Dy is amongst the most efficient magnetocaloric materials. Near the Néel temperature (179 K) $\Delta T = 12$ K for an applied field of 70 kOe [7,8]. For bulk Dy and external field strength less than 10 kOe, there are three temperature regions with qualitatively different MCE: (1) $\Delta T(H, T)$ is positive for low temperatures ($T < 120$ K), where the hexagonal anisotropy holds the spins in a ferromagnetic arrangement; (2) for moderately high values of T (160 K–170 K), where the helical phase is stable, $\Delta T(H, T)$ is negative; and (3) for temperatures close to 179 K, $\Delta T(H, T)$ is positive, because a small external field strength is enough to produce a ferromagnetic arrangement. The anomalous MCE of bulk Dy originates in the nature of its magnetic phases. For strong values of the external field strength Dy is either in the fan phase or ferromagnetic phase and has positive MCE, with negative values of $(\partial M(T, H)/\partial T)_H$ in most of the field interval in Eq. (3). For weak external field the helical state is stable from the Curie temperature up to Néel temperature and the MCE is negative close to the Néel temperature, with $(\partial M(T, H)/\partial T)_H > 0$.

One may anticipate that the field dependence of the MCE of thin Dy films is different from that of bulk Dy. The magnetic phases of Dy thin films may suffer relevant changes due to surface and finite-size effects, which introduce modifications of the exchange field acting on the spins in the near surface region. The stability of the helical state is modified, due to the lack of second neighbor spins in the near surface region, which favors the ferromagnetic alignment, and leads to new magnetic phases [9].

In this paper we show that it is possible to tailor the MCE of Dy by imposing geometrical constraints on the magnetic phases. We find that in ultra-thin films the confinement of spins in the direction perpendicular to the surface, inhibits the formation of the helical state. In the place of the helical state, the ferromagnetic arrangement is stable, from the Curie temperature up to the Néel temperature, and for any value of the external field strength. This leads to a significant enhancement of the MCE. The adiabatic temperature change, $\Delta T(T, H)$, for external field strength of the order of a few kOe, is much larger than what is found in bulk Dy, reaching $\Delta T/\Delta H = 6$ K/T for ultra-thin films.

We investigate a c-axis thin film, consisting of a stacking of atomic layers with equivalent spins, infinitely extended in the x–y directions. The spins in each monolayer are exchange coupled with the spins in the first and second neighbor monolayers. The anisotropy is uniform throughout the film and the near surface spins have reduced exchange energy. The magnetic Hamiltonian is given by

$$\mathcal{H} = J_1(g-1)^2 \sum_{n=1}^{N-1} \vec{J}(n).\vec{J}(n+1) + J_2(g-1)^2 \sum_{n=1}^{N-2} \vec{J}(n).\vec{J}(n+2) + \sum_{n=1}^{N} \{K_6^6 \cos(6\varphi_n) - g\mu_B \vec{J}(n).\vec{H}\}. \tag{4}$$

J_1 and J_2 describe the exchange interaction between the nearest and next nearest monolayers, $\vec{J}(n)$ denotes the total angular momentum per atom in the nth monolayer. K_6^6 describe the hexagonal anisotropy, and $\vec{H}$ is the external field, in the hexagonal plane. We use the Dy bulk energy parameters [10–13], $J = 15/2$, $J_1 = 44k_B$, $J_2 = -J_1/(4\cos\phi(T))$, where $\phi(T)$ is the temperature dependent helix turn angle [12]. $g = 4/3$, corresponding to a saturation magnetic moment per atom of $10\mu_B$, and $K_6^6(T)$, is adjusted so as to reproduce the temperature dependence [13] of the hexagonal anisotropy energy.

We use $|\vec{J}(n)| = J$, and the components of $\vec{J}(n)$ are $J_x(n) = J\cos(\varphi_n)$, $J_y(n) = J\sin(\varphi_n)$, φ_n is the angle with the x-axis in the hexagonal plane. The equilibrium configuration is the profile $\{\varphi_n; n = 1, \ldots, N\}$ that minimizes the magnetic energy. In equilibrium the torque on every spin $\vec{J}(n)$ is zero ($\vec{J}(n) \times (\partial\mathcal{H}/\partial\vec{J}(n)) = 0$). We have found that for a given value of the external field H there are several profiles that fulfill this condition. The equilibrium profile is selected as that which gives the lowest energy. We consider the external field in the basal plane, along one easy direction of the hexagonal anisotropy ($\varphi_H = 30°$), and we use a self-consistent local field algorithm, which allows calculating both the thermal average values ($\{\langle J(n)\rangle; n = 1, \ldots, N\}$), and the orientation of the spins in each layer ($\{\varphi_n; n = 1, \ldots, N\}$), taking into account the impact of the modifications of the exchange energy due to the reduced coordination near the surfaces [9].

The magnetic contribution to the specific heat was calculated from the difference in the magnetic energy for T and $T + \delta T$, where δT is a small increment in the value of the temperature [14]. The elastic contribution was calculated using a Debye model with a Debye temperature of $T_D = 158$ K [15]. Changes in the Debye temperature produce no impact in the results. Using $T_D = 172$ K, as found from heat capacity measurements at rather low temperatures [15], we have found that the fractional change in the elastic heat capacity for temperatures close to $T = 160$ K is smaller than 0.01.

Surface effects are incorporated since the spins near the surfaces have the exchange energy reduced by the absence of nearest and/or second nearest neighbors. The balance between the first neighbor ferromagnetic and the second neighbor antiferromagnetic exchange energies is modified for the spins of the first two planes near the surfaces ($n = 1, 2, N - 1$ and N). However surface effects are not restricted to the surface layers. The number of layers modified by the surface effects depends on the way the effective local field relaxes towards the bulk pattern in the middle of the film. Compared to bulk Dy, there are changes in the magnetic phases, and in the values of $(\partial M(T, H)/\partial T)_H$, affecting significantly the value of $\Delta T(T, H)$.

We have found that the magnetic phases of thick films resemble the bulk structure, apart from minor surface effects. However as the thickness is reduced the fraction of surface spins increases, and there are relevant changes in the magnetic phases. The surface modifications in the balance between ferromagnetic and antiferromagnetic exchange energies favors the stability of the ferromagnetic order along the hexagonal anisotropy easy directions, and leads to changes in the magnetization isotherms. We have found that the field strength required to saturate the magnetization decreases as the film thickness is reduced. Also, films much thinner than the helix period are ferromagnetic in the absence of external field, for any temperature from the Curie temperature up to the Néel temperature. This is a relevant issue regarding magnetocaloric (MC) properties. In this thickness limit the effect of the external field is similar to that found on ferromagnetic materials. $(\partial M(T, H)/\partial T)_H$ is negative for any value of the external field strength, and turns very large at the Néel temperature, for small values of H, leading to large values of $\Delta T(T, H)$.

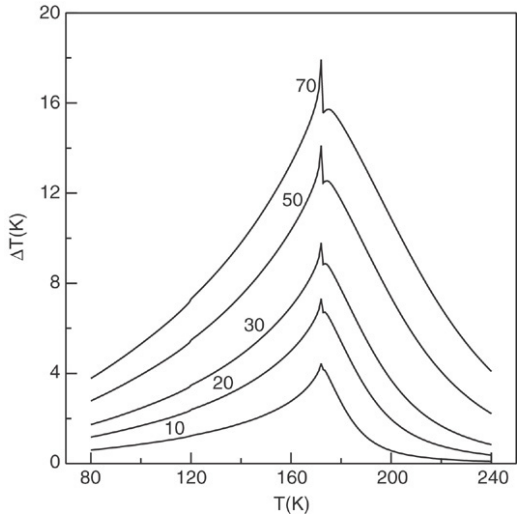

Fig. 1. Adiabatic temperature change of a 6 layer thick Dy film. The numbers by the curves indicate the value of H_f in kOe.

In Fig. 1 we show the adiabatic temperature change for a 6 layer Dy film, and external fields in the interval from 10 kOe to 70 kOe. The field dependence of the MCE is much stronger than for bulk Dy. Near the Néel temperature, and for $H = 7$ T, $\Delta T(T, H)$ is around 18 K. This value of $\Delta T(T, H)$ is 50% larger than that reported [7] for polycrystalline bulk Dy, for the same external field strength. Also, this large value of $\Delta T(T, H)$ is close to that reported recently [8], for single crystal Dy samples and an external field strength of 10 T. It is also seen in Fig. 1 that the MCE is relevant in a wide temperature interval. The large width of the $\Delta T(T, H)$ curve is a typical thin film effect. The near surface spins have smaller internal fields (reduced coordination), and are more affected by temperature than the inner spins. Their average thermal values deviates from saturation at lower temperature, leading to a broad temperature interval where $(\partial M(T, H)/\partial T)_H$ has a relevant value. Notice also from Fig. 1 that, for any temperature, $\Delta T(T, H) > 0$ for the chosen values of H, and that the values of $\Delta T(T, H)/\Delta H$ range from 4 K/T for $H = 1$ T to 2.7 K/T for $H = 7$ T. These are typical features of the MCE of ferromagnets, and might be of some interest for technical applications of Dy in MR. The finite size and surface enhancement of the field dependence of the MCE is largest for small field strengths because the order–disorder transition at the Néel temperature is sharp, and the values of $(\partial M(T, H)/\partial T)_H$ are large for small values of H.

We have found that the efficiency of the MCE effect of Dy films is thickness dependent. The field dependence of the MCE decreases continuously as the thickness increases, approaching the bulk pattern for thick films. Near the Néel temperature the bulk and thin film values of the helix turn angle are similar, $\phi(T) \backsimeq 40°$ [12]. Thus a complete helix corresponds to around nine atomic layers. One might then expect to find bulk MC properties for films with more than nine atomic layers. However, we have found that the surface effects persist until much larger films.

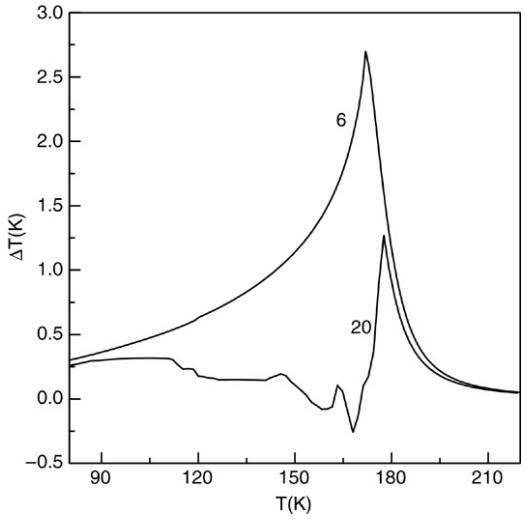

Fig. 2. Adiabatic temperature change of Dy films for $H = 5$ kOe. The numbers by the curves indicate the number of layers.

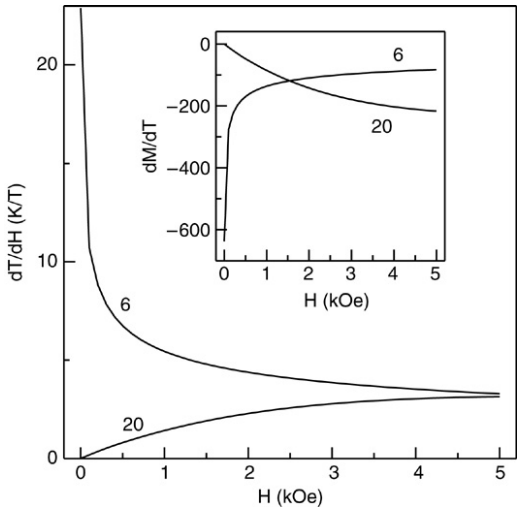

Fig. 3. The field derivative of the adiabatic temperature rise. The numbers by the curves indicate the number of layers. For each value of thickness the curves are drawn for the respective value of the Néel temperature: $T = 172$ K for the 6 layer film and $T = 177.6$ K for the 20 layer film. In the inset the corresponding values of $\mathrm{d}M/\mathrm{d}T$ are shown.

In Fig. 2 we show $\Delta T(T, H)$ for an external field of 5 kOe and for a 6 layer and a 20 layer film. We have chosen a small value of H because the thin film effects on the MC properties are more visible for small values of the external field. For large values of H, bulk Dy is either in the fan or ferromagnetic phase, with positive MCE, and except for the larger values of $\Delta T(T, H)$, thin films and bulk MC properties are similar. For the 20 layer film the peak in the MCE occurs at $T = 176$ K, with $\Delta T(T, H) \approx 1$ K. This is more than double the value measured for bulk Dy [7] for $H = 10$ kOe, which corrected for demagnetization effects is equivalent to a local field of strength $H \approx 6,6$ kOe [7]. It is also seen in Fig. 2 that the field dependence of the MCE for the 6 layer film is much larger, with $\Delta T(T, H) \approx 3$ K, for $T = 172$ K. This corresponds to $\Delta T(T, H)/\Delta H = 6$ K/T. This value is three times larger than the bulk value of $\Delta T(T, H)/\Delta H$ for a 7 T field. The thickness dependence of the MCE peak temperature is due to finite size effects in the Néel temperature, also found in other magnetic systems [16].

The key feature for thin film effects is the field dependence of the field derivative of the adiabatic temperature rise. As seen from Eq. (3), $(\mathrm{d}T/\mathrm{d}H)_H = -T(\partial M(T, H)/\partial T)_H/C(T, H)_H$. In Fig. 3 we show the field dependence of $(\mathrm{d}T/\mathrm{d}H)_H$, at the temperatures of the peaks of the adiabatic temperature change ($\Delta T(T, H)$), for a 6 layer film and a 20 layer film. The curves have been drawn for the temperatures of $T = 177.6$ K, for the 20 layer film, and $T = 172$ K for the 6 layer film. The ratio of almost three between the peak values of $\Delta T(T, H)$ shown in Fig. 2 result from the large differences of the $(\mathrm{d}M/\mathrm{d}T)_H$ curves shown in Fig. 3. The 6 layer film has a ferromagnetic behavior with a divergence of $(\mathrm{d}M/\mathrm{d}T)_H$ for $H = 0$, leading to the much larger value of ΔT.

The values of $\Delta T(T, H)$ at temperatures of the peaks in Fig. 2, for each film, are the areas under the corresponding $(\mathrm{d}T/\mathrm{d}H)_H$ curve in Fig. 3. As seen in Fig. 3, the difference of the MCE of the two films is larger as the value of the external field strength is smaller. We have found that for small values of the external field strength the field dependence of the heat capacity is rather weak. Thus, $(\partial M(T, H)/\partial T)_H$ is the leading factor for the field dependence of $(\mathrm{d}T/\mathrm{d}H)_H$.

In Fig. 4 we show the isofield magnetization curves for the 6 layer and the 20 layer films, and for small values of the external field strength. The curves correspond to external fields $H = 0$, 0.1 kOe, 0.2 kOe, 0.3 kOe, 0.4 kOe, 0.5 kOe and 0.6 kOe. Notice that the slope $(\partial M(T, H)/\partial T)_H$ of the curves for the 6 layer film at $T = 172$ K are much larger than the corresponding ones for the 20 layer film for $T = 176$ K, and the field effects in the 20 layer film are larger than in bulk Dy. For the chosen values of the strength of the external field, the magnetic phase of the 20 layer film is a distorted helix, as shown in the schematic representation of the spin structure for $H = 0.6$ kOe. As the temperature is raised there are changes in the spatial arrangement of the spins and in the thermal profile across the film, leading to a larger value of the net moment in the field direction compared to bulk Dy. The ferromagnetic arrangement of spins in the 6 layer film leads to large values of the total magnetic moment, with a saturation of $60\mu_B$ at low temperatures. The drop from around $14\mu_B$ at $T = 160$ K to nearly zero above the Néel temperature leads to the large MCE shown in Fig. 2.

We have shown that finite size and surface effects lead to considerable enhancement of the MCE of thin Dy films. Two features are worth noticing. First, the near surface spins are more easily turned in the direction of the external field. Near the surfaces the turn angle is smaller, due to the lack of second neighbors which favor a more ferromagnetic configuration. Thus, in thin films the external field strength required to modify the helical state is reduced. Second, the number of layers modified by the surface effects depends on the way of the effective local field relaxes from the surfaces towards the bulk pattern in the middle of the film. Thus, the finite size restrictions on the accommodation of the magnetic structure to the surface

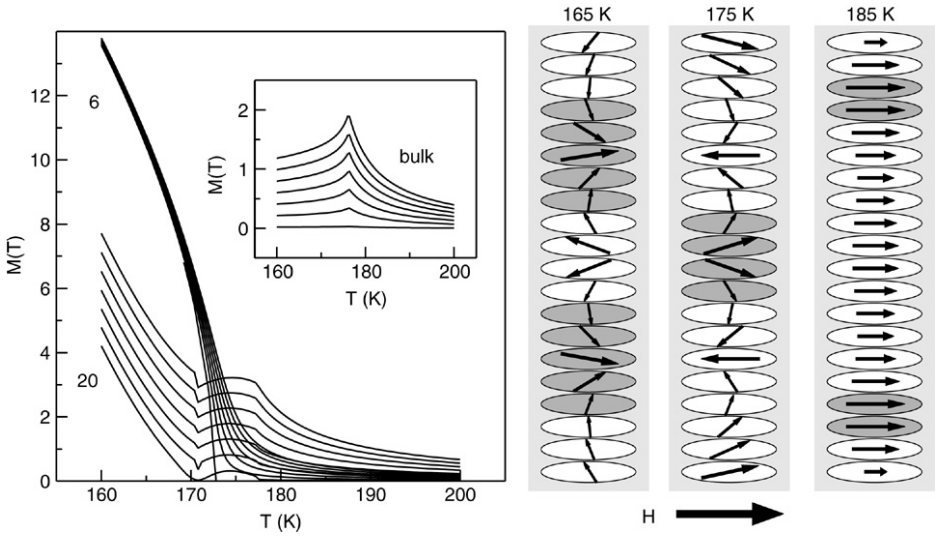

Fig. 4. Isofield magnetization curves for external field in the interval (0.0–0.6 kOe). The magnetization is shown in units of μ_B and the numbers by the curves indicate the numbers of layers. The bulk Dy magnetization curves are shown in the inset for the same external field values. A schematic representation of the spin structure in the 20 layer film, for $H = 0.6$ kOe at selected temperatures is also shown. The gray symbols indicate a slightly larger thermal value of the total angular momentum.

effects depend on the film thickness. A particularly critical case occurs for ultra-thin films. We have found that in this thickness limit there is not enough room for the helical state to form and the Dy film turns out to be a ferromagnetic arrangement of spins. This might be of technical interest since Dy has a large magnetic moment ($7.5\mu_B$ per atom) and thus a large MCE. We suggest that a system consisting of small Dy particles embedded in a non-magnetic matrix should display enhanced MCE, if the particle size is smaller than the helical period.

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