The Anisotropic Magnetocaloric Effect and Size-Dependent Magnetic Properties of Iron Particles

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Abstract
We present a theoretical study on the anisotropic magnetocaloric effect and the size-dependent magnetic properties of Fe particles of radii in the range 25–150 Å. An observable increase has been found in the magnetization, of the low radii (25–75 Å) particles, by reducing the temperature to 4 K. The anisotropic isothermal change in entropy \( \Delta S_m \) has been calculated by taking the difference between maximum \( \Delta S_m \) along the easy [100] and hard [111] directions. The maximum anisotropic \( \Delta S_m \) is 0.015 J/kg K for a field change of 500 Oe along the [100] direction. The \( \Delta S_m \) temperature dependence exhibits a table-like plateau for small radii (25–75 Å) and in low fields below 300 Oe. This enhances the relative cooling power (RCP) of the Fe element to be 8.11 J/kg for particles of 25 Å radius. Also, the calculation of anisotropic \( \Delta T_{ad} \) was performed along the easy axis and showed an increase in the maximum value around 37% relative to the experimental conventional value.

Keywords Ordinary magnetocaloric effect · Anisotropic magnetocaloric effect · Superparamagnetism · Size-dependent magnetization · Relative cooling power (RCP)

1 Introduction
Magnetocaloric effect (MCE) has attracted much research, both from the physics and application viewpoints, since its discovery in 1881 [1–8]. The discovery of the MCE in iron [9] has opened the door to extensive research on a variety of compounds, including the transition metal rare earth compounds, in an attempt to find the best MCE materials that operate near room temperature [1–15].

The fast development of nanometer-scale electronics demands the development of future cooling systems that can operate in complex geometries in the nanoscale range. An increase in the saturation magnetization in transition elements has been reported, when particle size is reduced to the nano-scale, at very low temperatures [15–17].

Research efforts, both experimental and theoretical, have been reported on the conventional MCE in the 3d transition elements at low and high fields, e.g., [14, 16, 18]. On the other hand, the anisotropic MCE (AMCE) is of interest because an increase in the entropy change could be achieved by rotating the crystal, along a specific crystalline direction, without changing the magnetic field intensity. This property was studied first by Kuzmin and Tishin in DyAlO3 [17].

The application of magnetocaloric materials, either ordinary or anisotropic, in magnetic refrigeration has been the subject of many papers [14, 18–23]; in particular, search for materials with magneto-volume coupling and first-order phase transition is currently an active research area. Other applications of MCE materials are in the domain of medicine, e.g., in treating hyperthermia and in drug delivery [15, 24–28], where nanoparticles could be used.

In the present work, we report on the anisotropic size-dependent magnetic properties and the anisotropic magnetocaloric effect of crystalline cubic Fe, for spherical particles of radii in the 25–150 Å range, and at temperatures up to \( T_c \). A statistical mechanics-based model is used, in the current work, for calculating the size-dependent magnetic and magnetocaloric properties of Fe. This model has been successfully used in studying a host of magnetic properties of magnetic systems of different crystalline symmetries. Examples of those systems are hexagonal, tetragonal, and...
mixed-anisotropy systems [29–33]. The aforementioned magnetic properties of those systems include magnetization curves, magnetic susceptibility, energy, torque, and probability landscapes.

2 Model and Analysis

The interplay between different magnetic energies dictates the magnetic properties of a given magnetic system and the total energy is subsequently used in evaluating magneto-thermal and magnetocaloric properties using the well-known relations of statistical mechanics.

Many publications provide experimental values of the temperature dependence of the anisotropy constants: $K_1$, $K_2$, and $K_3$ of Fe [34–40]. There is almost an agreement between these references on the sign and order of magnitude of $K_1$; however, this trend is not found regarding the value and the sign of $K_2$ and $K_3$. Therefore, we preferred to use the Callen and Callen power law [41, 42] to calculate the temperature-dependent anisotropy constants. The Callen and Callen law has been checked and verified for elements, e.g., Fe and Co [41–44]. The values of $K_1$ and $K_2$, at very low temperatures, used in our model were obtained from the reference by Getzlaff [40]. Those values proved to simulate low temperatures, used in our model were obtained from the reference [50] on the same subject.

In the reference by Pecharsky et al. [49], the authors discuss and comments on the analysis given in another specific crystalline direction. Equation (6) could be casted to take the following form [8, 44–49]:

$$\Delta S_m(T_{av}) = \frac{\delta H}{2\delta T}(\delta M_1 + 2 \sum_{k=1}^{n-1} \delta M_k + \delta M_n)$$  (7)

In the reference by Pecharsky et al. [49], the authors discuss the limitations that should be imposed on $\delta T$ and $\delta H$ in order for Eq. (7) to be valid. The same reference also discusses and comments on the analysis given in another reference [50] on the same subject.

![Fig. 1 The isothermal magnetization vs. magnetic field for Fe particles (r = 150 Å) at H = 800 Oe at room temperature. Our model (solid curves) experimental data (★ easy, · mid-hard, ○ hard directions)](image)
The adiabatic change in temperature for a specific change in the external magnetic field is given by many references, e.g., [4, 7, 8, 12]:

\[
\Delta T_{ad}(T, \Delta H) = - \int_{H_1}^{H_2} \frac{T}{C(T, H)} \frac{\partial M(T, H)}{\partial T} dH \tag{8}
\]

However, one may write Eq. (8) in the following approximate form if the heat capacity is weakly field-dependent [8, 12]

\[
\Delta T_{ad}(T, \Delta H) \approx - \frac{T}{C(T, H)} \Delta S_m(T, \Delta H) \tag{9}
\]

A figure-of-merit called the relative cooling power (RCP) has been introduced to assess the performance of magnetocaloric materials. The RCP is determined by multiplying the magnitude of the maximum \( \Delta S_m \) at a definite field, times the difference in temperature, at full width at half maximum, of the \( \Delta S_m \) vs. temperature curve as shown in the following equation [8] :

\[
RCP = \Delta S_{max} \times \frac{T}{\Delta T_{FWHM}} \tag{10}
\]

![Fig. 2](image) The isothermal magnetization curves at 300 K for Fe particle of different sizes at A 125 Å, B 100 Å, C 75 Å, D 50 Å, and E 25 Å
Results and Discussion

3.1 Size-Dependent Magnetization

Figure 1 shows the room temperature magnetization curves along the [100], [110], and [111] directions for a particle of radius $r = 150\, \text{Å}$ using our classical model. The saturation magnetization $M_s$ is about 1713 emu/cm$^3$ (220.17 emu/g), i.e., very close to the experimental value of 217.2 emu/g as reported by Coey [52] and Kittel [53].

The sequence of the easy [100], mid-hard [110], and hard [111] directions is in agreement with the well-known data on cubic Fe crystals, e.g., [53, 54]. We have studied the effect of particle size on the magnetization curves for particles in the size range of 25–150 Å at room temperature. Figure 2A–E show the dependence of the magnetization curves on particle size in the range 25–125 Å. We noticed a relative decrease in the anisotropy between the [100] and [111] directions as the particle size is reduced (e.g., Fig. 2C). For a particle size of 25 Å, as shown in Fig. 2E, the magnetization curves along the three directions become identical and saturation ($\sim 1700$ emu/cm$^3$) is far from being achieved in a field up to 800 Oe. Figure 3 displays the dependence of magnetization on particle size ($r = 25–150\, \text{Å}$), at 300 K and in 800 Oe field. The magnetization drops considerably as the particle size is reduced below about 50 Å. This behavior is consistent with the experimental results on Fe [55–57] and other particles like Gd [29]. Figure 4A–D shows the isothermal magnetization curves parallel to the easy [100] axis for particles with radii in the 25- to 150-Å range and at temperatures 600, 400, 150, and 4 K, respectively. The field required to achieve
saturation increases as the particle size decreases, for these three temperatures 600, 400, and 150 K.

In addition, for particle radii in the range 25–75 Å and at 4 K, a significant increase in the saturation magnetization has been achieved, e.g., for a radius of 25 Å, the magnetization is raised to ~1700 emu/cm³ as shown in Fig. 4D. This behavior is expected because thermal energy is insufficient, at low temperatures, to reduce the magnetization of extremely small particles, whereas this effect becomes more significant at high temperatures. A common feature of super-paramagnetic single-domain particles is that at high temperatures, the thermal energy overcomes the magnetic anisotropy energy barrier [29]. The most remarkable feature of superparamagnetism is shown in Fig. 5, namely the

![Fig. 5](image_url1) Fractional magnetization as function of \( H/T \) for a 25 Å particle at \( T=77, 150, \) and 200 K in a magnetic field up to 2 kOe

![Fig. 6](image_url2) Fractional magnetization as function of \( H/T \) for a 100 Å particle at \( T=100, 150 \) and 200 K in a magnetic field up to 1 kOe

![Fig. 7](image_url3) The isothermal AMCE \( \Delta S_{\text{ani}} \) for \( r=150 \) Å, in the temperature range from 900 to 1050 K for applied fields of A 50 Oe, B 100 Oe, C 300 Oe, and D 500 Oe
overlap of the M/Ms vs. H/T curves at 77, 150, and 200 K for the critical particle radius of 25 Å. The same behavior was previously pointed out in Fe, iron oxide–based alloys [58], and Gd element [29]. In contrast, Fig. 6 displays curves at temperatures 100, 150, and 200 K for size radius of 100 Å. The behavior confirms the ferromagnetic state for Fe particles [57].

### 3.2 Anisotropic Magnetocaloric Effect (AMCE)

The anisotropic MCE effect is manifested in the difference between the isothermal entropy changes calculated along different crystallographic directions in a field of constant magnitude [59, 60]. Figure 7A–D display the AMCE, using the trapezoidal method, in the field range 50–500 Oe, and at temperatures between 900 and 1050 K, for Fe particles of size 150 Å. The anisotropic $\Delta S_{\text{anis}}$ can be calculated by taking the difference between $\Delta S_m$ along the easy and hard directions. A large $\Delta S_{\text{anis}}$ is achieved in the low field region 50–500 Oe because the entropy of the spins is changed by application of a small field, in cluster and superparamagnetic materials more easily than in paramagnetic systems [61]. Table 1 shows the maximum value of $\Delta S_m$ at different fields 50, 100, 300, and 500 Oe for a radius of 150 Å. Figure 8 displays the temperature dependence of $\Delta S_m$ for $r=150$ Å in a field of 30 kOe. The maximum value is 8.36 J/kg K, along the easy axis, in comparison with 7.95 J/kg K for the bulk Fe [16]. So, the anisotropic MCE is enhanced over the ordinary MCE. Figures 9 and 10 display the size-dependent $\Delta S$, in a 1kOe field along the [100] direction for radii in the range 25–150 Å. A plateau feature [51] is found for 25-Å particles almost in the whole temperature range. Table 2 shows the RCP values for radii 50, 75, 100, and 150 Å in a field of 1 kOe. The highest value of RCP is 8.11 J/kg for a radius of 50 Å.

This behavior was reported previously in nano-sized Gd element by Miller [62] and Belo et al. [21]. However, the previous studies have not taken into account the calculation of anisotropic $\Delta T_{\text{ad}}$ and only the conventional $\Delta T_{\text{ad}}$ was presented experimentally as reported by [8, 15]. Based on Eq. (9), the anisotropic $\Delta T_{\text{ad}}$ is calculated along the easy direction [100] for applied field of 30 kOe. The heat capacity data was obtained from the experimental work presented in [8]. The anisotropic $\Delta T_{\text{ad}}$ has been calculated, using our model, with maximum value of 8 K as

| $H$ (Oe) | $\Delta S_m$ (J/K.kg) [100] | $\Delta S_m$ (J/K.kg) [111] | The maximum anisotropic $\Delta S_{\text{anis}}$ |
|----------|-----------------------------|-----------------------------|---------------------------------|
| 50       | 0.002                       | 0.001                       | 0.001                           |
| 100      | 0.011                       | 0.009                       | 0.002                           |
| 300      | 0.037                       | 0.022                       | 0.015                           |
| 500      | 0.112                       | 0.096                       | 0.016                           |

Fig. 8 The isothermal AMCE $\Delta S_{\text{anis}}$ for $r=150$ Å, in the temperature range from 900 to 1050 K for applied fields at 30 kOe along [100]

Fig. 9 $\Delta S_{\text{anis}}$ vs. temperature at $H=1$kOe, along [100], for particles of sizes in the 25–150 Å range

Fig. 10 The AMCE vs. temperature at $H=1$kOe for particles of sizes of 25, 75, and 150 Å along [100] direction
The statistical mechanics model proved to be fairly suitable for calculating the magnetothermal, magnetic size-dependent, and anisotropic magnetocaloric properties of the iron element.

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**Data Availability** This manuscript has no associated data or the data will not be deposited. The reader may contact me through my email: (eldocahmed4@gmail.com).

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**Table 2** The relative cooling power RCP for Fe particles of different radii along the easy axis [100] for a field of 1 kOe

| r (Å) | δT_{FWHM} | ΔS_{Max} (J/K.kg) | RCP (J/kg) |
|-------|------------|--------------------|-----------|
| 50    | 135        | 0.06               | 8.11      |
| 75    | 65         | 0.12               | 7.80      |
| 100   | 38         | 0.18               | 6.84      |
| 150   | 23         | 0.25               | 5.75      |

**Fig. 11** The adiabatic AMCE ΔT_{ad} along [100] easy axis for r=150 Å, in the temperature range from 1000 to 1050 K for applied fields of 30 kOe compared to the conventional experimental ΔT.

The size-dependent magnetization curves for Fe particles showed a ferromagnetic behavior at room temperature, for radii in the 50–150-Å range. Particles with a smaller radius, about 25 Å, exhibit a super-paramagnetic behavior. The isothermal change in entropy for field change in the 50–500-Oe range showed an anisotropy in the ΔS_{m} behavior for field applied along the [100], [110], and [111] axes. The particles in the 25-Å size range exhibit a plateau in its temperature dependence of ΔS_{m}. The adiabatic change in temperature ΔT_{ad} along the [100] axis, in a 30-kOe field, is about 37.5% larger than the experimental value. The lack of experimental data on C_{total}(T, H) does not enable us to calculate ΔT_{ad} without the use of the approximation form of Eq. (9).
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