



Magnetic phase transitions and giant magnetocaloric effect of EuTiO₃ nanowires



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ABSTRACT

An improved phenomenological thermodynamic theory is used to investigate the magnetic phase transitions and magnetocaloric effect of EuTiO₃ nanowires by considering the radius of the nanowires and the surface tensions. We are surprised that a transition mode from paramagnetic to ferromagnetic skipping antiferromagnetic phase can appear directly in the EuTiO₃ nanowires by increasing surface tension coefficients or decreasing nanowires radius. Moreover, a giant magnetocaloric effect of $\Delta S = 155.1$ J/kgK and $\Delta T = 23.5$ K can be obtained in this transition process for $R = 0.8$ nm nanowires under the applied magnetic fields change of 15 T, suggesting the potential application of EuTiO₃ nanowires in low-temperature magnetic refrigeration.

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1. Introduction

The researches of magnetic refrigeration based on the magnetocaloric effect (MCE) of magnetic materials have attracted great attention because of its high energy-efficiency and environment-friendliness compared with traditional gas compression refrigeration [1–4]. The investigations on MCEs mainly focus on the alloys of rare earth elements and their compounds, the materials with perovskite or perovskite-like structures, and multiferroic compound. Some materials exhibiting large MCEs at low temperature or close to room temperature have been discovered, such as La(Fe, Si)₁₃ [5], Mn_{5-x}Ge₃Ni_x [6], MnFeP_{1-x}As_x [7], HoMnO₃ [8], as well as Ni-Mn-In and Ni-Co-Mn-In etc magnetic shape memory alloys [9,10]. However, the magnetic adiabatic temperature changes of the obtained materials are still not large enough and difficult to be utilized in the commercial application.

EuTiO₃ (ETO) is one of the multiferroic ABO₃ perovskite members presenting the G-type antiferromagnetism (AFM) and

quantum paraelectricity in bulk. For heteroepitaxial thin films or nanoparticles of ETO compound, the experimental and theoretical investigations have discovered that the coexistence of ferroelectric and ferromagnetic (FM) order can occur in its single phase and induce some novel physical properties due to lattice mismatch or surface tension [11,12]. We have recently also reported the electrocaloric effects of ETO nanowires and thin films by using phenomenological thermodynamic theory to reveal the influence of external applied stress (including tensile and compressive) on electrocaloric properties [13,14]. Whereat, a large electric field-induced adiabatic temperature change has been predicted near room temperature. So we have reason to believe that a large and tunable MCE may be also obtained since ferroelectric and magnetic order can coexist in single phase ETO nanowires. Furthermore, although there have been lots of researches on the magnetic and electrical properties of ETO compound [15,16], the investigations on the MCEs of ETO nanowires are scarce.

Since electronic spin orders of Eu ion exhibit AFM/FM transition under the applied stress or surface tension in ETO nanowires [12], their magnetic phase transitions and MCEs must be related to the surface tension, applied stress and applied magnetic field. In the present paper, the magnetic transitions and MCEs of ETO nanowire are considered basing on an improved Landau phenomenological thermodynamic theory. The controls of surface tension and applied magnetic field on magnetic and MC properties of ETO nanowires

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with different radius are investigated in detail. A giant MC effect is achieved at transition temperature, where the magnetic entropy change ΔS can reach about 155.1 J/kgK and the adiabatic temperature change ΔT can reach 23.5 K in ETO nanowires with $R = 0.8$ nm when a magnetic fields change of 15 T is applied. These results are much higher than the previous results obtained in many other MC materials and EuTiO_3 bulk.

2. Theoretical analysis

The ETO compounds present different magnetic orders under the different size and different temperatures according to previous investigations, for convenience, we here consider an ETO nanowire with length h and radius R ($h \gg R$), to investigate its magnetic transitions and MCE. In view of the possibility that the inherent surface tension can induce the FM and AFM order in ETO nanowires, magnetic sublattice a and b are assumed. The magnetization vector then can be written as $M = (M_a + M_b)/2$, and the antiferromagnetic magnetization vector as $L = (M_a - M_b)/2$, and total free energy of ETO nanowire can be given by:

$$F = F_V + F_S, \quad (1)$$

where F_V is the energy of bulk part and F_S the one of surface part. For the bulk part, Landau–Ginzburg–Devonshire (LGD) free energy F_V can be expressed as [14,17]:

$$F_V = 2\pi \int_0^h \int_0^R \left(\beta_{1M} M^2 + \beta_{2M} M^4 + \beta_{3M} M^6 - Z_{11} \sigma_1 M^2 - Z_{12} (\sigma_2 + \sigma_3) M^2 + \beta_{1L} L^2 + \beta_{2L} L^4 + \beta_{3L} L^6 - \tilde{Z}_{11} \sigma_1 L^2 - \tilde{Z}_{12} (\sigma_2 + \sigma_3) L^2 + \lambda L^2 M^2 - \frac{1}{2} S_{11} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) - S_{12} (\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_1 \sigma_3) - MH \right) r dr dz. \quad (2)$$

Here, coefficients β_{iM} , β_{iL} ($i = 1, 2, 3$) are magnetic stiffness and high order stiffness coefficients, and $\beta_{1M} = \beta_C(T - T_C)$, $\beta_{1L} = \beta_N(T - T_N)$, and T_C , T_N are Curie and Neel temperatures, respectively. For equivalent arranged magnetic Eu ions with antiparallel spin ordering, we can assume that $\beta_C = \beta_N$. σ_i ($i = 1, 2, 3$) is inherent stress tensor, and an isotropic approximation $\sigma_1 = \sigma_2 = \sigma_r$ is used according to the symmetrical structure of ETO nanowires. Based on the mechanical equilibrium conditions and the appropriate boundary condition $\sigma_r = -\mu/R$, and μ is the effective surface tension coefficient. The external stress σ_3 is along z direction determined by the applying force f , and $\sigma_3 = f/\pi R^2$. In the following discussion, we assume that f is zero without applying force. The coefficient λ reflects the coupling between M and L . S_{ij} is elastic compliance. Z_{ij} , $\tilde{Z}_{ij}$ are magnetostrictive and antimagnetostrictive coefficients, respectively. H is the applied magnetic field.

The surface energy F_S of ETO nanowires has the form as:

$$F_S = \frac{1}{2} \int_S \alpha_M^S M^2 dS + \frac{1}{2} \int_S \alpha_L^S L^2 dS = \frac{1}{2} \int_S \left(\frac{\delta}{\lambda_M} M^2 + \frac{\delta}{\lambda_L} L^2 \right) dS. \quad (3)$$

Here, we assume that surface energy coefficient $\alpha_{M,L}^S = 0$ and neglect the surface effects because of no reliable experimental data, although the intrinsic surface stress can favor the long range spin ordering in the nanosized system [18]. In this case, the uniformly distributional magnetization and strain distributions are almost independent of polar coordinate r but can correlate to the nanowire

radius R [17,18]. Therefore, surface tension plays an extremely important role in the control of magnetic state of the nanowires.

Depending on the thermodynamic equilibrium conditions $\partial F/\partial M = 0$ and $\partial F/\partial L = 0$, magnetization M and AFM magnetization L can be derived, and MC coefficient m at given magnetic field H and stress σ can also be obtained as follows:

$$m = \left(\frac{\partial(M, L)}{\partial T} \right)_{H, \sigma}. \quad (4)$$

Then, according to the Maxwell relation $(\partial \Delta S / \partial H)_{T, \sigma} = (\partial(M, L) / \partial T)_{H, \sigma}$, the entropy change ΔS and adiabatic temperature change ΔT can be expressed as:

$$\Delta S = \int_{H_1}^{H_1 + \Delta H} \left(\frac{\partial(M, L)}{\partial T} \right)_{H, \sigma} dH, \quad (5)$$

$$\Delta T = -\frac{T}{C\rho} \int_{H_1}^{H_1 + \Delta H} \left(\frac{\partial(M, L)}{\partial T} \right)_{H, \sigma} dH, \quad (6)$$

where C , ρ are the specific heat capacity and mass density for ETO nanowires, respectively, and H_1 is the initial magnetic field. Thus, the influence of nanowires radius, the surface tension and the applied magnetic field on the MCE can be investigated. All the used parameters are given in Table 1.

3. Results and discussions

First, since the ECE is usually strong close to the magnetic phase transitions, the case of transitions for ETO nanowires at different surface tension and with different radius is of great importance. Fig. 1 illustrates the variation of spontaneous magnetization (M/L) of the ETO nanowires and two kinds of their phase transition modes: PM/FM, PM/AFM/FM. It is shown from Fig. 1(a) and (b) that for the ETO nanowires with surface tension coefficient $\mu = 10$ N/m, spontaneous magnetizations (M/L) increase with decreasing

Table 1
Values of parameters for EuTiO_3 nanowires [11,13,17,19].

Parameter	Unit	Value
LGD-coefficients	Henri/(m·K)	$\beta_C \approx \beta_N = \pi \times 10^{-6}$
	Jm/A ⁴	$\beta_{2M} = 0.2 \times 10^{-16}$
	Jm/A ⁴	$\beta_{2L} = 0.33 \times 10^{-16}$
	Jm/A ⁴	$\beta_{3M} = \beta_{3L} = 0$
AFM Neel temperature	K	$T_N = 5.5$
FM Curie temperature	K	$T_C = 3.5$
Magnetostriction coefficients	m ² /A ²	$Z_{11} = -5.25 \times 10^{-16}$
		$Z_{12} = 8.75 \times 10^{-16}$
		$\tilde{Z}_{11} = -5.25 \times 10^{-16}$
		$\tilde{Z}_{12} = 7.75 \times 10^{-16}$
Elastic compliances	m ² /N	$S_{11} = 3.62 \times 10^{-12}$
		$S_{12} = -0.87 \times 10^{-12}$
Specific heat capacity	J/(kgK)	$C = 44.35$
Mass density	kg/m ³	$\rho = 6.15 \times 10^3$

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