Modelling of magnetostructural transitions in MM'X magnetocaloric compounds

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This work presents a Landau-type theory to describe the hexagonal-orthorhombic magnetostructural phase transition and the stability regions in MM'X compounds. By minimizing a thermodynamic potential based on strain tensor components, the theory facilitates the analysis of phase transition stability. The Gibbs free energy analysis is used to calculate the field-induced entropy change during the magnetostructural transition, with theoretical results compared to experimental data.

Keywords: martensitic transformation; magnetostructural phase transition; magnetocaloric effect; Landau theory.

1. Introduction

Many MM'X compounds for magnetocaloric applications exhibit a first-order martensitic transition from a high-temperature hexagonal austenitic phase to a low-temperature orthorhombic martensitic phase [1]. The structural martensitic transition temperature is typically higher than the Curie temperature. Alloying MM'X compounds aims to couple structural and magnetic phase transitions, achieving a first-order magnetostructural transition from paramagnetic austenite to ferromagnetic martensite to maximize the magnetocaloric response [2]. However, the coupling of first-order structural and second-order magnetic phase transitions leads to the appearance of thermal hysteresis, which is undesirable for the practical applications. To minimize hysteresis in magnetostructural transitions, the first-order structural transition should be analyzed. This work develops a Landau-type theory to describe the hexagonal-orthorhombic phase transition and the stability regions of austenitic and martensitic phases, linked to thermodynamic hysteresis [3].

2. Results and discussion

The structural phase transition is analyzed using Landau theory, which minimizes a thermodynamic potential expanded in terms of an order parameter, composed from the strain tensor components [4,5]. The hexagonal-orthorhombic transition is represented by the following simplified elastic free energy:

$$F_{el} = \frac{1}{4}(C_{11}+C_{12})(\eta_0^0)^2 + \frac{1}{2}C_{33}(\eta_1^0)^2 + C_{13}\eta_0^0\eta_1^0 + \\ + \frac{1}{2}A(T)(\eta_2^2+\eta_5^2) + \frac{1}{2}B(\eta_2^3 - 3\eta_2\eta_5^2) + \frac{1}{4}C(\eta_2^2+\eta_5^2)^2, \quad (1)$$

where the components of order parameter $\eta_2 = \varepsilon_{xx} - \varepsilon_{yy}$ and $\eta_5 = \varepsilon_{xy}$ correspond to the deviatoric and shear strains during phase transition, while concomitant components $\eta_0^0 = \varepsilon_{xx} + \varepsilon_{yy}$ and $\eta_1^0 = \varepsilon_{zz}$ correspond to volume change during transition. The constants C_{11}, C_{12}, C_{33}, C_{13} are elastic moduli, while phenomenological constants A, B, C can be determined from the values of C_{11}, C_{12} and lattice parameters of martensitic and austenitic phases (see e.g. [5]). The temperature dependence of coefficient $A(T)$ determines the stability regions these phases: the condition $A(T_2) = 0$ corresponds to the limit of stability of austenitic hexagonal phase, while $A(T_1) = B^2/4C$ corresponds to the limit of stability of martensitic orthorhombic phase.

The developed approach was applied to the MnNiGeFe alloy, which undergoes a hexagonal-orthorhombic phase transition. Measured lattice constants and elastic moduli computed from *ab initio* were used to estimate energy coefficients. Figure 1 shows the free energy as a function of strain at different temperatures, revealing two minima corresponding to the hexagonal and orthorhombic phases. Depending on the temperature, the system stabilizes in one of the two minima. At the equilibrium temperature T_{eq}, both phases have equal energy but remain separated by an energy barrier.

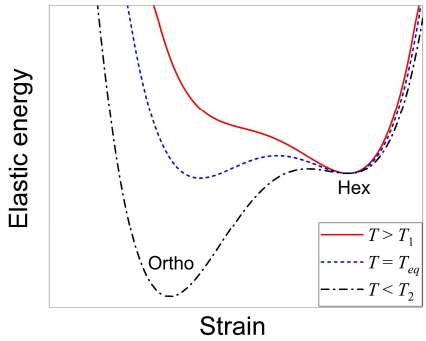

Figure 1: Elastic free energy as a function of strain computed for temperatures above the limit of stability of orthorhombic phase (red line), below the limit of stability of hexagonal phase (black line) and at equilibrium temperature (blue line)).

The analysis of Gibbs free energy, including elastic, magnetoelastic, and magnetic terms, enables the calculation of field-induced entropy change during a magnetostructural phase transition [6].

References

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