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The Role of First and Second Order Phase Transitions in MnCoGe-Based Compounds: Implications for Magnetic Refrigeration Technology

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ABSTRACT

This review presents a comprehensive analysis of MnCoGe-based compounds and their potential for magnetic refrigeration applications, focusing on the phase transitions and magnetocaloric properties of these materials. MnCoGe-based alloys exhibit both first and second-order phase transitions, with first-order transitions delivering large magnetic entropy changes (ΔS_M) but also suffering from thermal hysteresis. Second-order transitions, though offering smaller entropy changes, provide improved thermal stability and reduced hysteresis, making them suitable for continuous operation. Compositional tuning, through the addition of elements such as Si, Al, and Fe, has been shown to optimize the magnetocaloric performance of these materials, particularly by tailoring the transition temperature to practical levels. Performance evaluation highlights the significant cooling capacities of MnCoGe-based compounds, indicating their potential for energy-efficient and environmentally friendly magnetic refrigeration systems. The paper concludes with recommendations for future research, emphasizing the need for further optimization of material properties and the development of scalable synthesis methods for industrial applications.

Keywords: *MnCoGe-based compounds; magnetocaloric effect; phase transitions; magnetic refrigeration; thermal hysteresis*

1. Introduction

Magnetic refrigeration technology has garnered significant attention in recent years due to its potential to provide energy-efficient and environmentally friendly cooling solutions. Unlike conventional vapor-compression refrigeration systems that rely on harmful refrigerants and energy-intensive processes, magnetic refrigeration leverages the magnetocaloric effect (MCE) to achieve cooling. In this process, the application or removal of a magnetic field to magnetocaloric materials induces a reversible temperature change, allowing for precise and controllable cooling without the need for harmful gases or chemicals [1-3]. This makes magnetic refrigeration an attractive alternative for reducing environmental impact and enhancing energy efficiency in cooling systems.

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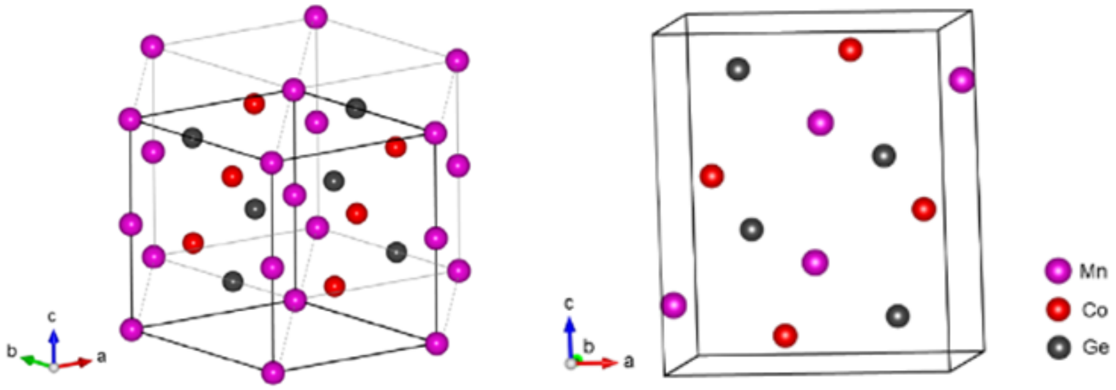
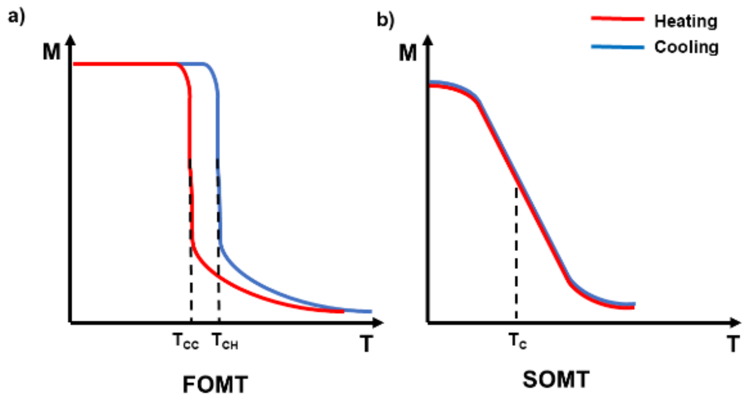
One of the most promising candidates for magnetic refrigeration applications is the family of MnCoGe-based compounds. These intermetallic materials exhibit complex magnetic and thermal behaviors, with notable magnetocaloric properties due to the unique interactions between their magnetic, electronic, and structural components [1,2]. MnCoGe-based compounds possess either hexagonal Ni2In-type or orthorhombic TiNiSi-type crystal structures (shown in Figure 1), which significantly influence their magnetic ordering and phase transitions [3,4]. The inclusion of transition metals like manganese (Mn), cobalt (Co), and germanium (Ge) further enhances these materials' magnetic performance, including ferromagnetic and antiferromagnetic transitions, as well as the ability to switch between metallic and semiconducting states depending on temperature and composition [5,6]. This versatility makes MnCoGe-based compounds highly relevant for next-generation refrigeration systems, offering both high cooling capacity and energy efficiency.



(a) (b)

Fig. 1. The crystallographic unit cells of MnCoGe-based alloys (a) hexagonal Ni2In-type structure (*P63/mmc*, austenitic phase) and (b) orthorhombic TiNiSi-type structure (*Pnma*, martensitic phase) based on database in materialsproject.org

A critical factor in the performance of these compounds lies in their phase transitions. Magnetic refrigeration relies heavily on the magnetocaloric effect, which is amplified during phase transitions in magnetic materials. In MnCoGe-based compounds, both first and second-order phase transitions play a crucial role in determining the strength of the MCE. First-order transitions, often characterized by abrupt changes in structure and magnetism, tend to exhibit larger entropy changes and, consequently, higher cooling capacities as shown in Figure 2 [7]. On the other hand, second-order phase transitions are typically more gradual and continuous, resulting in lower hysteresis and greater thermal stability during operation [16]. Understanding the nature of these transitions and how they affect the magnetocaloric properties of MnCoGe-based compounds is therefore essential for optimizing their performance in real-world refrigeration applications.



(a) (b)

Fig. 2. Schematic of M vs T plot for MCM exhibiting (a) First-order magnetic transition and (b) Second-order magnetic transition

Research has shown that the composition and structural modifications of MnCoGe-based materials can significantly impact the nature of their phase transitions and magnetocaloric properties [4,5]. Substituting certain elements or fine-tuning the microstructure via advanced synthesis methods, such as mechanical alloying and spark plasma sintering, can help modulate the magnetic ordering and phase transition characteristics, making it possible to tailor these materials for specific applications [6,7,8]. Recent studies have focused on enhancing the performance of MnCoGe-based compounds for magnetic refrigeration, exploring both their first and second-order transitions to maximize the MCE while minimizing energy losses and material degradation over time.

The significance of MnCoGe-based compounds in magnetic refrigeration stems from their unique ability to exhibit giant magnetocaloric effects due to their complex phase transition behavior. By understanding and optimizing these phase transitions, researchers aim to develop materials that provide high-efficiency cooling for a variety of energy applications, including heat pumping and waste heat recovery systems [6]. This study contributes to the ongoing effort to evaluate the magnetic and thermal properties of MnCoGe-based compounds, with a focus on their phase transitions and overall performance in magnetic refrigeration applications.

2.1 Experimental Setup

Various characterization techniques were employed to study the synthesized compounds' structural, thermal, and magnetic properties for magnetocaloric materials especially MnCoGe-based compounds. X-ray diffraction (XRD) analysis was used to determine the samples' crystal structure and lattice parameters [9,10]. The XRD patterns were further refined using Rietveld analysis, which helped remove impurity peaks and provide detailed information on lattice parameters.

Differential scanning calorimetry (DSC) was utilized to study phase transitions [3], which measured the heat flow associated with the structural transitions. This technique allowed for the determination of the latent heat and the structural transition temperature, which are critical for understanding the magnetocaloric behavior of the materials. Unlike magnetic measurements, DSC is not affected by external magnetic fields, making it a valuable tool for evaluating thermal transitions independently.

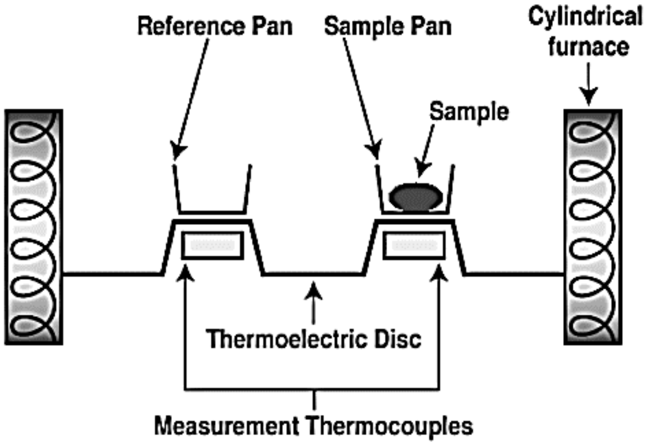


Fig. 3. DSC sample chamber containing the reference and the sample pan with the heating module

Magnetic measurements were conducted using a Physical Property Measurement System (PPMS) equipped with a vibrating sample magnetometer (VSM). This system provided precise data on the magnetic properties, such as magnetization as a function of temperature and field, helping to assess the magnetocaloric effect (MCE) in the MnCoGe-based compounds [11,12]. The PPMS was operated under various conditions, including sweeping the magnetic field from 0 to 5 T and measuring isothermal magnetization curves at intervals of 2 K or 4 K around the Curie temperature (Tc). The PPMS also allowed for high-temperature measurements up to 1000 K, extending the range of thermal and magnetic characterization.

The key parameters evaluated during the performance analysis included entropy change (ΔS_M), adiabatic temperature change (ΔT_{ad}), hysteresis losses, and thermal stability. These parameters are critical for assessing the potential of MnCoGe-based compounds for magnetic refrigeration applications. The magnetocaloric effect was evaluated by calculating the change in magnetic entropy (ΔS_M) using the numerically integrated form of Maxwell's equation. This approach allowed for the accurate determination of the magnetic entropy change over a range of applied fields, with values up to 5 T.

Hysteresis losses, a common issue with first-order transitions, were carefully examined by performing magnetization measurements for both increasing and decreasing fields. The absence of significant hysteresis in the MnCoGe-based compounds indicated that second-order phase transitions dominated, which is advantageous for reducing energy losses during magnetic refrigeration cycles. Thermal stability was also evaluated by examining the structural transitions using DSC and XRD to confirm that the materials could maintain their properties over repeated thermal cycles.

Additionally, the refrigeration capacity (RC) was calculated as a metric for performance. RC was derived from the product of the maximum entropy change and the temperature span at the full width at half maximum (FWHM) of the ΔS_M versus temperature curve. This parameter provides an estimate of the heat transfer between hot and cold reservoirs during an ideal refrigeration cycle, making it a critical performance indicator for magnetocaloric materials.

Thermodynamic modeling and critical exponent analysis were used to predict material behavior and provide a deeper understanding of the phase transitions observed in MnCoGe-based compounds. These computational methods helped simulate the magnetic and thermal properties of the materials, providing insights into how composition and structure modifications could influence the magnetocaloric effect. By combining experimental results with computational models, the study aimed to optimize the material properties for specific magnetic refrigeration applications, ensuring that the compounds not only exhibited high MCE but also operated efficiently under realistic conditions.

3. Results

3.1 Phase Transition Characterization

The magnetocaloric effect (MCE) in MnCoGe-based compounds is driven by both first and second-order magnetic transitions (FOMT and SOMT). First-order magnetic transitions are characterized by a coupled magneto-structural transformation, where a sharp phase change occurs between the low-temperature ferromagnetic state and the high-temperature paramagnetic state. This abrupt change in structure results in large magnetic entropy changes (ΔS_M) at the transition temperature, making FOMT materials attractive for high-efficiency cooling applications [13]. For example, MnCoGe compounds demonstrate a significant magneto-structural transition, where the ferromagnetic phase at lower temperatures transitions sharply to a paramagnetic phase upon heating [14]. This sharp transition yields a large ΔS_M, enhancing the cooling potential. However, this first-order transition is typically accompanied by thermal hysteresis, which is a major challenge in maintaining the operational efficiency of magnetic refrigeration systems.

In contrast, second-order magnetic transitions involve a more gradual change between ferromagnetic and paramagnetic phases, leading to a smoother variation in magnetization with temperature [21]. SOMT materials like pure Gd exhibit lower magnetic entropy changes compared to FOMT materials but offer better thermal stability and reduced hysteresis, which can be advantageous for continuous operation in refrigeration systems. MnCoGe-based compounds exhibit both FOMT and SOMT, depending on their composition and structural modifications, allowing for tunability of the magnetocaloric effect for specific applications [36].

3.2 Magnetocaloric Properties

The magnetocaloric properties of MnCoGe-based compounds are influenced by the nature of the phase transition, as well as by compositional tuning and processing conditions. Comparative analysis shows that compounds exhibiting first-order transitions generally deliver larger ΔSM values. For instance, MnCoGe alloys doped with elements such as Si, Al, and Fe demonstrate significant improvements in ΔS_M due to the enhanced magneto-structural coupling [15,16]. In these materials, the entropy change can be as high as 10 $Jkg^{-1}K^{-1}$ for moderate magnetic field changes, indicating their potential for magnetic refrigeration applications [17].

However, while first-order materials provide high cooling efficiencies, second-order materials, such as those based on Fe, Ni, and Gd, offer improved operational stability. Gd, for instance, exhibits a ΔS_M value of 4.2 $Jkg^{-1}K^{-1}$ at a transition temperature of 294 K, making it suitable for near-room-temperature applications, despite its relatively lower cooling capacity compared to FOMT materials [18]. Therefore, MnCoGe-based compounds, which can demonstrate both first and second-order transitions depending on their specific composition, are highly versatile and can be tailored to meet different refrigeration performance requirements.

3.3 Material Stability and Hysteresis

A significant challenge associated with first-order magnetocaloric materials is thermal hysteresis, which arises due to the latent heat required to drive the coupled magnetic and structural transition. This hysteresis, characterized by a temperature difference between the heating (T_{CH}) and cooling

(T_{CC}) cycles, leads to energy losses and reduced operational efficiency [19]. For MnCoGe-based compounds, thermal hysteresis is a notable issue, as materials exhibiting sharp first-order transitions tend to suffer from hysteresis losses during repeated cooling cycles. The value of hysteresis loss (ΔT_{Hyst}) can be calculated as the difference between T_{CH} and T_{CC}, with larger hysteresis leading to more pronounced energy dissipation and reduced material performance in practical applications [19].

In contrast, second-order magnetic transitions generally exhibit minimal or no hysteresis, making them more attractive for continuous magnetic refrigeration systems. For instance, the SOMT in Gd and Fe-based alloys results in negligible hysteresis, allowing for more efficient operation over multiple thermal cycles [20]. This makes SOMT materials particularly suitable for applications requiring stable, long-term performance, although they may not offer the same magnitude of cooling efficiency as their FOMT counterparts.

3.4 Optimization Strategies

To improve the performance of MnCoGe-based compounds for magnetic refrigeration, several optimization strategies can be employed. One common approach is compositional tuning through the substitution of alloying elements. For example, adding elements such as Si, Al, and Cr to MnCoGe has been shown to modulate the transition temperature and enhance the magnetocaloric effect [15,21-23]. This tuning allows researchers to tailor the phase transition to occur closer to room temperature, where magnetic refrigeration systems are most efficient. Additionally, adjusting the alloy composition can help reduce thermal hysteresis, as seen in $Mn_{1-x}CoGe$ alloys, which exhibit improved MCE properties and reduced hysteresis when vacancy tuning or element substitution is employed [16].

Another strategy involves refining the microstructure of the materials through advanced processing techniques such as ball milling, melt spinning, and annealing. These methods help improve the homogeneity of the material and optimize the distribution of magnetic domains, thereby enhancing the magnetocaloric performance. Annealing MnCoGe-based compounds at high temperatures in a vacuum, for instance, has been shown to improve phase purity and reduce the formation of secondary phases that can detract from the magnetocaloric effect [7].

Incorporating additional elements such as Co into $La(Fe, Si)_{13}$ alloys has also been explored to improve material performance, specifically by increasing the Curie temperature (T_C) and reducing the hysteresis [24]. Similar strategies can be applied to MnCoGe-based systems, where the inclusion of transition metals or rare earth elements may improve the operational range and stability of the materials.

4. Conclusion

The study of MnCoGe-based compounds reveals that these materials exhibit both first and second-order phase transitions, which significantly influence their magnetocaloric properties. First-order transitions, characterized by sharp magneto-structural changes, lead to large magnetic entropy changes (ΔS_M), making these materials highly effective for magnetic refrigeration applications. However, these transitions also present challenges due to thermal hysteresis, which can reduce efficiency. Second-order transitions, on the other hand, offer better thermal stability and minimal hysteresis, though with smaller entropy changes. The performance evaluation indicates that MnCoGe-based compounds, particularly those doped with elements such as Si, Al, and Fe, demonstrate promising magnetocaloric behavior, with high cooling capacities and reduced energy losses. MnCoGe-based materials hold significant potential for industrial-scale magnetic refrigeration systems due to their ability to exhibit large magnetocaloric effects and tunable transition temperatures. With further optimization, these materials could offer energy-efficient, environmentally friendly alternatives to conventional refrigeration technologies. The combination of tunable phase transitions and enhanced magnetocaloric performance positions MnCoGe-based alloys as promising candidates for large-scale cooling applications.

Future research should focus on further optimizing the material properties of MnCoGe-based compounds, particularly by reducing thermal hysteresis and enhancing structural stability through compositional tuning and microstructural refinement. Additionally, scaling up production techniques, such as advanced alloying methods and improved synthesis processes, will be essential for bringing these materials closer to commercial viability. Further studies should also explore long-term performance and the integration of MnCoGe-based materials into functional magnetic refrigeration devices.

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