Coherent spin rotation-induced zero thermal expansion in MnCoSi-based spiral magnets

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Abstract

Materials exhibiting zero thermal expansion (ZTE), namely, volume invariance with temperature change, can resist thermal shock and are highly desired in modern industries for high-precision components. However, pure ZTE materials are rare, especially those that are metallic. Here, we report the discovery of a pure metallic ZTE material: an orthorhombic Mn1-xNixCoSi spiral magnet. The introduction of Ni can efficiently enhance the ferromagnetic exchange interaction and construct the transition from a spiral magnetic state to a ferromagnetic-like state in MnCoSi-based alloys. Systematic in situ neutron powder diffraction revealed a new cycloidal spiral magnetic structure in the bc plane in the ground state, which transformed to a helical spiral in the ab plane with increasing temperature. Combined with Lorentz transmission electron microscopy techniques, the cycloidal and helical spin order coherently rotated at varying periods along the c-axis during the magnetic transition. This spin rotation drove the continuous movement of the coupled crystalline lattice and induced a large negative thermal expansion along the a-axis, eventually leading to a wide-temperature ZTE effect. Our work not only introduces a new ZTE alloy but also presents a new mechanism by which to discover or design ZTE magnets.

Introduction

It is well known that the inherent anharmonicity of phonon vibrations triggers the volume expansion of most solids upon heating. However, when the crystalline lattice couples with ferroelectricity, magnetism, and charge transfer, anomalous behavior during large temperature fluctuations, namely, negative thermal expansion (NTE) behavior, may be realized1–4. Combining NTE materials with positive thermal expansion (PTE) materials can reduce the overall coefficient of thermal expansion (CTE) and lead to overall zero thermal expansion (ZTE) composites, which are of great importance in industrial applications as structural components, electronic devices, and high-precision instruments5–7. Unfortunately, such ZTE composite materials have high internal stresses that can cause microcracking during thermal cycling, which significantly diminishes their mechanical performance and lifetime. This problem can be overcome with single-phase ZTE materials with homogeneous internal structures, especially in metallic form. In addition to Invar alloys8, a small number of such single-phase ZTE alloys and compounds have been discovered thus far, such as Mn1-xCoxB9, YbGaGe10, LaFe10.5Si2.411, Ho2Fe16Cr12, ErFe10V1.6Mo0.413, and RFe2-based compounds14–16.

The most common of these materials are magnetic alloys, for which the ZTE behavior is intimately associated with spontaneous magnetic ordering, known as the magnetovolume effect (MVE). The MVE originating from spin–lattice coupling may weaken or even compensate for anharmonic lattice variations and lead to abnormal thermal expansion behavior near the magnetic ordering temperature17,18. Here, we present a new class of ZTE materials, MnCoSi-based metamagnetic alloys, consisting of a homogeneous phase. The ternary equiatomic MnCoSi
alloy crystallizes with an orthorhombic structure from a honeycomb hexagonal structure after experiencing a martensitic transition at high temperature (Fig. 1 and Supplementary Fig. S1). The shortest Co–Si bonds yield wrinkled eight-membered rings, in which Mn–Mn zig–zag chains are embedded. The interconnected Co–Si contacts along the [100] direction form the basic rigid skeleton. Due to the critical nearest Mn–Mn separation, MnCoSi alloys possess a ground state of nonlinear antiferromagnetism (AFM) and a magnetic-field-induced magnetoelastic transition 19,20, during which a large inverse magnetocaloric effect and giant magnetostrictive effect are realized21–23. In this study, we find that the helical magnetic structure of MnCoSi, as is widely recognized, transforms to cycloidal spiral AFM at low temperature. Moreover, we report that when the MnCoSi system is tuned by minimal Ni introduction, an ultralow CTE over a wide temperature range can be achieved. The combination of X-ray diffraction (XRD), neutron powder diffraction (NPD), and Lorentz transmission electron microscopy (TEM) techniques reveal a new mechanism underlying ZTE: coherent spin rotation of the spiral magnetic structures.

Materials and methods
Sample synthesis
Polycrystalline Mn1-xNi_xCoSi (x = 0, 0.010, 0.015, 0.017, 0.020, and 0.025) samples were prepared by arc melting the appropriate amounts of high-purity raw materials under a purified argon atmosphere three times. Then, the as-cast samples were sealed in evacuated quartz ampoules and annealed at 1123 K for 60 h before being slowly cooled to room temperature over 72 h. The slow-cooling treatment guaranteed magnetic homogeneity 24.

Magnetization, XRD, and NPD characterization
The magnetic properties were characterized by a superconducting quantum interference device (SQUID, Quantum Design MPMS XL7) with the reciprocating sample option. The temperature dependence of the powder XRD (Rigaku, Smartlab) was collected using a low-temperature chamber. For each measurement at a specified temperature, the powder sample was maintained for 20 min to reach heat equilibrium. In situ variable-temperature NPD measurements (\(\lambda = 1.622\) Å) in the heating process were carried out on the Wombat beamline at the OPAL facility of the Australian Nuclear Science and Technology Organization (ANSTO). Structural refinements of the XRD and NPD patterns were performed using the Rietveld refinement method, and the irreducible representation analysis of the magnetic structure was carried out using the BASIREPS program, both implemented in the FULLPROF package 25,26.

Lorentz TEM measurements
The thin plates for Lorentz TEM observations were prepared with a focused ion beam. The temperature dependence of the magnetic domain structures was observed in a JEOL-dedicated Lorentz TEM (JEOL2100F) equipped with liquid-nitrogen holders. To determine the in-plane spin distribution of the magnetic texture, three sets of images with under, over, and just (or zero) focal lengths were recorded with a charge-coupled device (CCD) camera, and then the high-resolution in-plane magnetization distribution map was obtained using the commercial software QPt on the basis of the transport-of-intensity equation (TIE) equation. The orientation of the in-plane magnetization was depicted based on the color wheel. The crystalline orientation for the thin plate was determined by selected area electron diffraction (SAED).
Results

According to the atomic occupancy rules in MnCoSi alloys\textsuperscript{23}, when Ni atoms nominally substitute for Mn atoms, Ni with more valence electrons preferably occupies the Co site, and then a partial Co atom occupies the Mn site. Thus, the occupation formula of the Mn\textsubscript{1-x}Ni\textsubscript{x}CoSi system should be written as (Mn\textsubscript{1-x}Co\textsubscript{x})(Co\textsubscript{1-x}Ni\textsubscript{x})Si. The atomic occupation can also be confirmed by NPD refinement, as shown in Supplementary Fig. S2. Based on the atomic occupation, the lattice parameters and unit-cell volume of the Mn\textsubscript{1-x}Ni\textsubscript{x}CoSi system are obtained from the refinement of XRD patterns, as shown in Fig. 2. For further details of the refinement, see Supplementary Fig. S3 and Supplementary Table S1. With decreasing temperature, the lattice parameters \(b\) and \(c\) typically decrease, while the lattice parameter \(a\) shows an NTE effect. Moreover, with the introduction of Ni, the expansion of the lattice parameter \(a\) upon cooling shifts to a low temperature and changes dramatically. As a result, the effect of the shrinkage of \(b\) and \(c\) on the unit-cell volume is compensated for; thus, ZTE behavior is realized in Ni-containing samples, as presented in Fig. 2d. The reliability of anisotropic thermal expansion and ZTE can also be confirmed from the NPD results (Supplementary Fig. S4). Notably, stoichiometric MnCoSi exhibits a linear PTE in the studied temperature range with a slight inflection at \(\sim 230\) K. When Ni substitutes for minimal Mn, the samples, such as those with contents of \(x = 0.020\) and 0.025, exhibit ultralow CTEs (\(\alpha_l = 6.9 \times 10^{-7}\) and \(1.3 \times 10^{-7}\) \(\text{K}^{-1}\), respectively) over a wide temperature range (10–190 K and 10–170 K, respectively) after experiencing a normal PTE and a weak NTE, respectively, that are approximately one-order smaller than that of the Invar alloy of Fe\textsubscript{65}Ni\textsubscript{35} (\(\alpha_l = 1.4 \times 10^{-6}\) \(\text{K}^{-1}\)). The calculated CTEs and corresponding working temperature ranges are listed in Supplementary Table S2 in the Supplementary Materials.

As mentioned before, the thermal expansion properties of magnetic materials can be affected by the MVE. The temperature dependence of the magnetization (\(M\)–\(T\)) curve during zero-field cooling (ZFC) and field cooling (FC) processes in Fig. 3a and Supplementary Fig. S5 shows that the weak magnetization of nonlinear AFM increases slowly with increasing temperature; this behavior is interrupted by the advent of paramagnetism (PM) in stoichiometric MnCoSi alloys. Hence, the long-range magnetic order cannot be maintained above \(T_0 \sim 387\) K, where \(T_0\) represents the order-to-disorder transition temperature. It is widely reported that the introduction of external elements can effectively tune the magnetic state of TMnX (\(T = \) transition metal, X = Si or Ge) alloys\textsuperscript{19,27}. In this work, the M–T curves of the studied Mn\textsubscript{1-x}Ni\textsubscript{x}-CoSi system indicate that minimal Ni addition strengthens the ferromagnetic (FM) interaction, leading to a rise
in the hidden thermal-induced magnetic transition similar to that in Fe-substituted MnCoSi alloys. For the \( x = 0.020 \) sample, the AFM state smoothly transitions to the FM-like state, which is accompanied by a relatively large increase in magnetization. The magnetic transition temperature \( T_x \), defined as the inflection point in the M–T curve, is presented in Supplementary Table S2 in the Supplementary Materials and gradually decreases with increasing Ni content. In addition, the establishment of FM coupling can be examined by the magnetization curve, is presented in Supplementary Table S2 in the Supplementary Materials and gradually decreases with increasing Ni content. In addition, the establishment of FM coupling can be examined by the magnetization behavior. As shown by the room-temperature magnetization curves in Fig. 3b, the metastable nonlinear AFM can be easily destroyed by applying a magnetic field. A second-order and nonhysteretic metamagnetic transition displaying a sharp increase in magnetization is clearly seen in stoichiometric MnCoSi and tends to saturate at \( B_{sat} \sim 3.0 \) T. With increasing Ni content, \( B_{sat} \) decreases (Supplementary Table S2), and the field-induced magnetism vanishes for the \( x = 0.020 \) and 0.025 samples, where only FM-like behavior is exhibited. The macroscopic magnetic measurements indicate that the introduction of Ni can trigger a magnetic transition from the weak nonlinear AFM state to the FM-like state, where NTE or ZTE emerges.

To further determine the evolution of the magnetic structure, the temperature-dependent NPD was performed on the Mn\(_{1-x}\)Ni\(_x\)CoSi system. In the NPD patterns of the studied \( x = 0.000, 0.015, \) and 0.020 samples in Fig. 4 and Supplementary Fig. S6, with decreasing temperature, additional peaks at low diffraction angles corresponding to the magnetic satellite reflections gradually appear and then split or merge, manifesting the possible AFM order. Specifically, the refinement of isothermal NPD data at selected temperatures is also shown. At 450 K, only the nuclear scattering of the orthorhombic space group is indexed because the sample is in a disordered paramagnetic state. When the sample enters the spin-ordered state below \( T_x \), the magnetic reflections can be indexed by the nonlinear magnetic structure. As the temperature further decreases lower than 190 K for sample \( x = 0.020 \), magnetic diffraction peaks of \((101)^\perp\), \((-101)^\perp\), \((202)^\perp\) and \((-202)^\perp\) at \( \sim 2\theta = 18^\circ \) and 40° gradually become prominent, which may be indicative of the change in the nonlinear magnetic structure.

Assisted by symmetry arguments, the best-fit model indicates that ordered and equal moments are detected on Mn atoms (\( \sim 5\) \( \mu_B \)) or Co atoms (\( \sim 0.6\) \( \mu_B \)) (Supplementary Fig. S7) at 3 K, for which the cycloidal spiral magnetic arrangement lying in the \( bc \) plane achieves an incommensurate propagation vector \( k = (0, 0, k_z) \) for the \( x = 0.020 \) sample, as shown in Fig. 5a, b. This spiral magnetic structure is different from the helical magnetic structure in the literature (two NPD refinements are presented and discussed in Supplementary Fig. S8), which was also reported by O. Baumfeld before. Specifically, although all the atoms occupy the same crystal site (Wyckoff position 4c (\( x, 1/4, z \))), the wave vector group splits the magnetic Mn and Co positions into four magnetic spirals with identical \( k \) values: \( <\text{Mn1, Mn3}, \), \( <\text{Mn2, Mn4}, \), \( <\text{Co1, Co3}, \), and \( <\text{Co2, Co4}, \), and the magnetic spin in each cycloidal spiral rolls with a fixed angle along the \( c \)-axis. As the main carriers of the magnetic moment, the two magnetic spirals of Mn atoms exhibit obvious phase differences, indicating different spin orientations in the \( x = 0.020 \) sample at the ground state. As the temperature increases, the four groups of cycloidal AFM transform to four groups of helical magnetic structures at approximately 190 K for the \( x = 0.020 \) sample. As illustrated in Fig. 5c, d, the spin in each helix of the helical magnetic structure rotates in the \( ab \) plane by a certain angle from layer to layer along the \( c \)-axis. Therefore, the envelope of the projection of magnetic moments in the \( bc \) plane is sinusoidally modulated, as shown in Fig. 5c. At 300 K, the two Mn helices rotate almost synchronously and show a small phase difference in the \( x = 0.020 \) sample.

Figure 6 shows the related angles between different magnetic spins from the analysis of NPD refinement. Based on their atomic positions, the nearest Mn or Co atoms in
each helix have z-coordinates that differ by 0.5, implying a phase difference of $k_c/2$ between spins and an angle between the adjacent Mn or Co atoms of $180^\circ k_c$. With a temperature increase from 3 to 350 K, the propagation vector component $k_c$ of the cycloidal or helical AFM structure for the studied samples decreases, with a relatively abrupt change near $T_t$ (Fig. 6a), indicating a decrease in the angle between the adjacent spins ($\theta_{\text{Mn1-Mn3}}/\theta_{\text{Mn2-Mn4}}$) in a cycloidal or helical magnetic chain and, correspondingly, an elongation of the magnetic spiral period. The temperature-dependent $\theta_{\text{Mn1-Mn3}}$ shows more obvious variation in Ni-containing samples, and the angle...
θ_{Mn1-Mn3} is further reduced (i.e., 23° at 300 K for the x = 0.020 sample). Moreover, the phase analysis, as shown in Fig. 6b, indicates that the angle between the nearest atoms of two Mn cycloidal or helical spirals (θ_{Mn1-Mn2}) decreases (i.e., 19° at 300 K for the x = 0.020 sample). Consequently, the spins of all Mn atoms tend to continuously rotate toward the parallel arrangement of the b-axis, as shown in Fig. 6c; d, thus, an FM-like spin configuration is expected in Ni-containing samples.

In addition, Lorentz TEM is widely employed to investigate the real-space imaging of spiral magnetic structures.\(^{31,32}\) We imaged the magnetic domain structures in the x = 0.020 sample using Lorentz TEM under a zero magnetic field between 140 K and 300 K, as shown in Fig. 7 (details are shown in Supplementary Fig. S9). The studied thin specimen is near the \([1–10]\) zone axis orientation confirmed by the SAED in the inset. At 293 K, uniform and nanosized fine magnetic patterns with bright and dark contrast are repeatedly arranged perpendicular to the c-axis. Based on the over- and underfocused Lorentz TEM images (Supplementary Fig. S9), a TIE was used to characterize the spin textures of the magnetic patterns. The yellow and blue straight stripe pairs reflect the regions with opposite in-plane magnetic inductions, as indicated by the color wheel. Together with the line profile of the alternative contrast intensity, the nearly sinusoidal changes in the inductions indicate that the spin order is probably spiral or fan-like. Note that only the in-plane component of moments is presented by the Lorentz TEM. Therefore, the real 3D magnetic structures of this thin MnCoSi specimen should be resolved systematically by in situ Lorentz TEM in the future. The fine stripe-type magnetic domain can be observed in the studied temperature ranges of 140–293 K. With increasing temperature, the width of the stripe increases. In addition, the spiral magnetic structure, which contains a higher harmonic modulation of magnetic order, clearly provides a pair of diffraction spots along the c-axis close to the (000) diffraction spots of SAED, as shown in the inset of Fig. 7b. Through quantitative analysis of these satellite spots, the
magnetic spiral period can be calculated, as shown in Fig. 7b. As the temperature increases, the period gradually increases and accelerates at ~220 K, which is consistent with the NPD data and further validates the coherent rotation of the magnetic spins.

**Discussion**

Near-ZTE behavior has been mentioned in terms of or observed in MnCoSi-based alloys,[20,33] while the origin of the effect was not discussed. The conventional mechanism underlying ZTE or NTE in magnetic alloys, such as La (Fe,Si)_{13} alloys and RFe_{2} based compounds,[11,14–16,34,35], originates from either a magnetic disorder to order transition or a large change in the magnetic moment.

Here, to quantitatively uncover the contribution of magnetism to the thermal expansion behavior of the Mn_{1-x}Ni_{x}CoSi system, the spontaneous volume magnetostriction $\omega_{m}$ of sample $x = 0.020$ is calculated by subtracting the contribution of the nonmagnetic part ($\omega_{nm}$) from the experimental thermal expansion data ($\omega_{exp}$). By using the Debye–Grüneisen model[36,37], as shown in Fig. 8a. Combined with the M–T curve (Fig. 8b), the sample displays linear PTE behavior in the PM region. When the sample starts to enter the ordered FM-like state at below 410 K, the experimental $\omega_{exp}$ slightly deviates from the fitted $\omega_{m}$ due to the MVE.

With a further decrease in the temperature, a smooth magnetic transition from the FM-like state to the spiral...
AFM state is observed, during which the thermal expansion behavior is significantly affected. Specifically, the negative role of magnetic $\omega_m$ gently exceeds or completely counteracts the contribution from the lattice variation, which results in a weak NTE and a wide-temperature ZTE. Moreover, $\omega_m$ and the angles between Mn spins exhibit similar temperature-dependent behavior (Fig. 8c), which indicates an intimate relationship between the anomalous thermal expansion and spin rotation of the helical magnetic structure in MnCoSi-based alloys.

Notably, thermally induced coherent spin rotation is also observed in stoichiometric MnCoSi. During heating, the angles $\theta_{Mn1-Mn3}$ and $\theta_{Mn1-Mn2}$ decrease from 70° and 61° to 38° and 32°, respectively. Then, the rotation is forced to cease by the disordered PM state. Therefore, this weak and partial spin rotation brings about only a small fluctuation in the thermal expansion behavior of stoichiometric MnCoSi (shown in Fig. 2d), for which a PTE is observed over the entire temperature range. The unusual magnetic tricritical behavior of MnCoSi results in flexible tunability of the magnetic state. It is widely reported that the magnetic state of this Mn-based orthorhombic alloy with space group $Pnma$ is extremely sensitive to the Mn–Mn distance $d_l$. In this work, the introduction of Ni atoms can produce “chemical pressure” on the crystal lattice and change $d_l$. As shown in Fig. 8d, $d_l$ increases with increasing Ni content; correspondingly, nonlinear AFM tends to be FM. Therefore, the enhanced FM interaction leads to an obvious transition from the cycloidal or helical AFM state to an FM-like state, during which the magnetic spins further coherently rotate to the $b$-axis. Due to robust magnetoelastic coupling, this strong rotation gives rise to giant spontaneous magnetostriction, particularly the sharp contraction of the $a$-axis, and leads to the emergence of anomalous NTE or ZTE behavior in the homogeneous phase. In addition, our results suggest that an appropriate internal or external stimulus, such as doping with elements, introducing vacancies or applying hydrostatic pressure or a magnetic field, can strengthen the FM interaction and establish this spiral AFM-FM-type transition, inducing ZTE in MnCoSi-based alloys.

Note that the change in magnetic structure from cycloidal to helical spiral cannot be clearly revealed in the evolution of lattice parameters and magnetic properties of polycrystalline samples. Due to the intimate relations between the magnetic state and Mn–Mn separation, an evident step change of $d_l$ (Fig. 8d) can be observed that corresponds to the change in the spiral AFM structure in the MnCoSi-based alloy. In addition, owing to the distinct easy magnetization planes of cycloidal ($bc$ plane) and helical ($ab$ plane) spirals, the magnetic structures can be effectively distinguished by magnetic characterization of MnCoSi single crystals.

Conclusions

In summary, a wide-temperature ZTE effect and a new cycloidal spiral AFM structure were found in orthorhombic Mn$_{1-x}$Ni$_x$CoSi alloys. Systematic magnetic measurements and in situ XRD, NPD, and Lorentz TEM characterization indicated that the introduction of Ni can enhance the FM interaction and induce a transition from the spiral AFM state to an FM-like state. During this transition, the spin lying in the $bc$ or $ab$ plane rotates uniformly, leading to drastic changes in the lattice parameters due to magnetoelastic coupling, which results in ZTE behavior. Moreover, this new mechanism sheds light on magnetic materials that possess this spiral AFM-FM-type transition, and ZTE or NTE materials may be discovered or designed.

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Author contributions

J.L. and W.W. proposed the idea and designed the experiments. J.L. and B.D. prepared the samples. B.D. and Y.Y. performed TEM and analyzed the related data. J.L. and W.W. wrote and developed the manuscript. B.D. and Y.Y. performed TEM and analyzed the related data. J.L. and B.D. performed the NPD. J.L., J.W., and G.W. analyzed the NPD results.

Conflict of interest

The authors declare no competing interests.

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