Supporting information

# Giant negative thermal expansion in bonded MnCoGe-based compounds with $Ni_2In$-type hexagonal structure

Ying-Ying Zhao†, Feng-Xia Hu†*, Li-Fu Bao†, Jing Wang†*, Hui Wu‡,§, Qing-Zhen Huang‡, Rong-Rong Wu†, Yao Liu†, Fei-Ran Shen†, Hao Kuang†, Ming Zhang†, Wen-Liang Zuo†, Xin-Qi Zheng†, Ji-Rong Sun†, Bao-Gen Shen†

† Beijing National Laboratory for Condensed Matter Physics and State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China

‡ NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

§Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, USA

* To whom correspondence should be addressed. E-mail: fxhu@iphy.ac.cn; wangjing@iphy.ac.cn

Series title:

I. Neutron diffraction measurements on structure
II. Compared M-T curves for bonded and as-prepared samples
III. Sample bonding process and SEM measurements

## I. Neutron diffraction measurements on structure

To precisely investigate the details of lattice change during phase transition, we performed neutron powder diffraction studies on the crystal and magnetic structures. Figure S1 (a) and (c) depict the evolution of the unit cell volumes and phase fractions with temperature, together with the magnetic moments of orthorhombic phase, for the as-prepared $MnCoGe_{0.99}In_{0.01}$ with magnetostructural coupling. It is noticeable that with the disappearance of magnetic ordering the sample undergoes a structural transformation from the orthorhombic martensite (space group: *Pnma*) to the hexagonal austenite (space group: *P6₃/mmc*). Meanwhile, an abrupt unit cell volume drop of $\Delta V/V=(V_{ortho}/2-V_{hex})/V_{hex}\approx 3.9\%$ occurs (Note: the unit-cell of the two phases has the relationship $V_{ortho} = 2V_{hex}$ [V. Johnson, *Inorg. Chem.* **14**, 1117-1120 (1975).]). This fact evidences that a transition occurs between FM orthorhombic and PM hexagonal structure. From Figure S1(a), the average unit cell volume $\overline{V}$ as a function of temperature can be straightly obtained, as shown in Figure S1(b). For comparison's sake, here we defined the transition window as the region where negative slope of $\overline{V}$-$T$ occurs. For the as-prepared $MnCoGe_{0.99}In_{0.01}$ without binders, the starting and end temperature is ~270K and ~330K, respectively, and the width of phase transition window is ~60K, as indicated in Figure S1(b). Such a wide phase transition window has been regarded as a result of thermodynamic equilibrium-type martensitic transition in some previous researches[13].

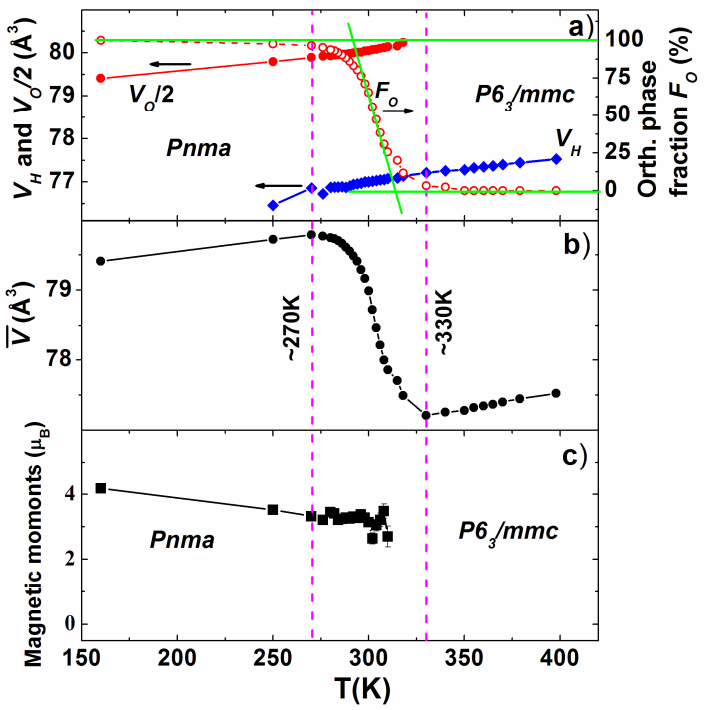


Figure S1. Since the number of the chemical formula per unit cell is 4 for the orthorhombic phase and 2 for the hexagonal phase, a half of the orthorhombic cell volume $V_O/2$ is used to compare with the hexagonal unit cell volume $V_H$ in the plot. (a)Unit cell volume of hexagonal phase ($V_H$, blue rhombus), half of unit cell volume of orthorhombic phase ($V_O/2$, red solid circle) and orthorhombic phase fraction ($F_O$, red empty circle), (b) average unit cell volume, and (c) magnetic moments of the orthorhombic phase as a function of temperature for the as-prepared $MnCoGe_{0.99}In_{0.01}$.

II. Compared M-T curves for bonded and as-prepared samples

Figure S2 (a) and (b) present the compared M-T curves (temperature dependent magnetization) measured under a magnetic field 0.3T for the bonded and as-prepared compositions with and without magnetostructural coupling. From Figure S2 and the dM/dT plots in the insets, one can distinguish the significant broadening of the structural/magnetostructural transformation ($T_{stru}$/$T_{mstru}$) while the pure magnetic transition around $T_C$ keeps unchanged for the bonded samples. The $T_{mstru}$ shifts by 10K (from 321K to 311K) for the bonded $MnCoGe_{0.99}$ with magnetostructural coupling, while for the decoupled $Mn_{0.97}In_{0.03}CoGe$ with separated $T_{stru}$ and $T_C$, the $T_{stru}$ shifts by 7K (from 226K to 219K) while $T_C$ keeps unchanged (261K). The significant broadening of the structural/magnetostructural transformation enforced by the residual stress governs the NTE behavior in the bonded samples.

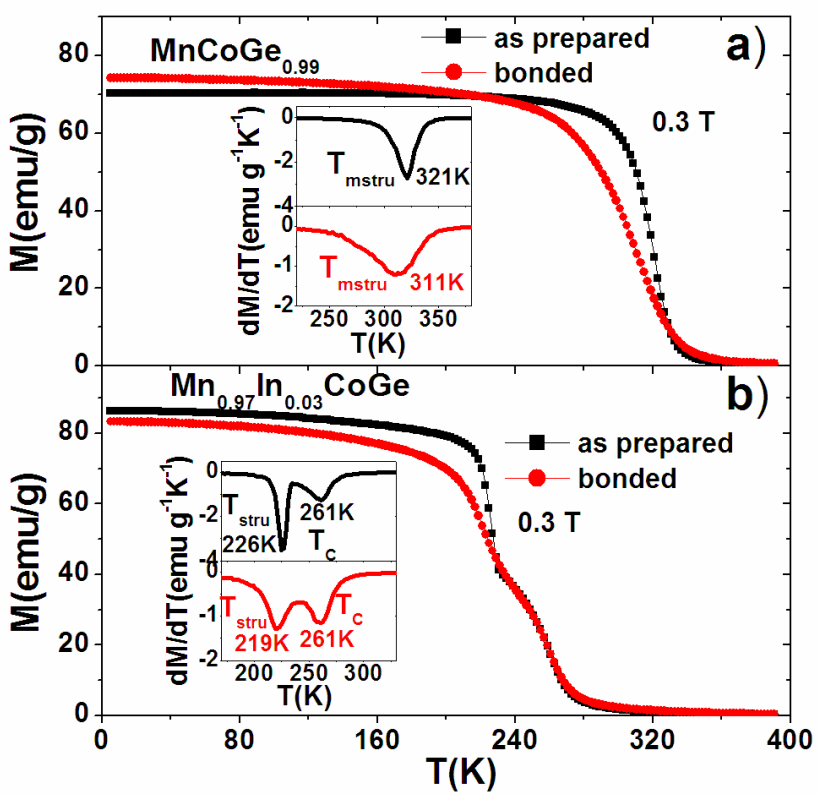


Figure S2. The comparison of temperature dependent magnetization under 0.3T for the bonded and as-prepared compositions (a) $MnCoGe_{0.99}$ with magnetostructural coupling and (b) $Mn_{0.97}In_{0.03}CoGe$ with separated $T_{stru}$ and $T_C$. The insets show the corresponding dM/dT plots.

III. Sample bonding process and SEM measurements

A few percents of epoxy plus hardening agent, totally 3-4wt%, (or silver epoxy plus hardening agent, 6wt% in total) were introduced and evenly mixed with the powders. Then, the mixture was loaded into a mould (in a shape of cylinder with a diameter of 5 mm) made of high chromium carbide alloy tool steel and press formed under a pressure

of 11.5kbar for 2 min, and then loaded in an oven and solidified at 170°C for 30min in vacuum($1\times10^{-3}$Pa), eventually resulted in the bonded alloys. To know the distributions of the epoxy binder in the sample, we chose the bonded $Mn_{0.97}In_{0.03}CoGe$ and performed scanning electron microscope (SEM) and energy disperse spectroscopy (EDS) measurements by Helios Nanolab 600I and Hitachi-S4800. The results indicate that the $Mn_{0.97}In_{0.03}CoGe$ particles (the grey areas) are wrapped by epoxy (the black areas), as shown in Figure S3. The porosities among the particles are also indicated in Figure S3.

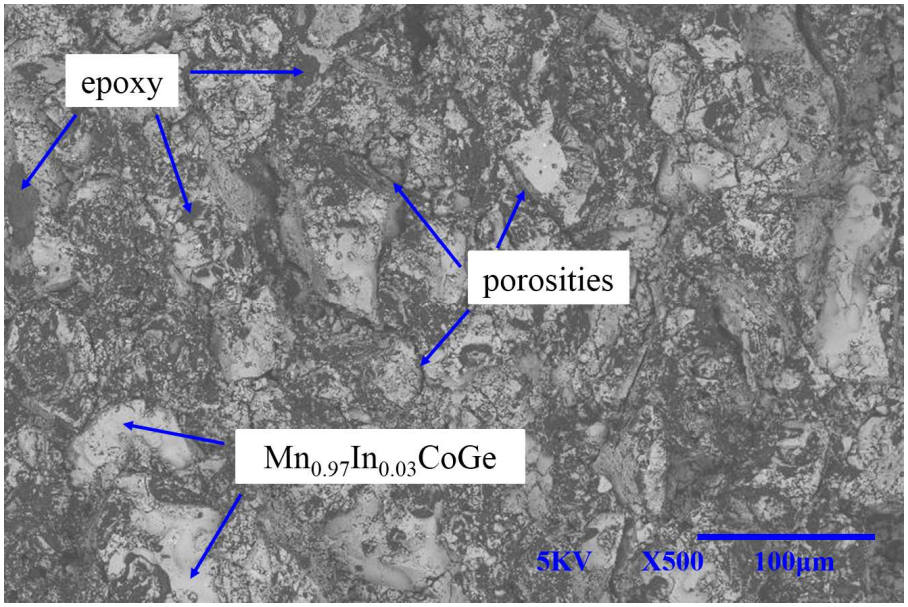


Figure S3. Backscattered SEM micrographs of the bonded $Mn_{0.97}In_{0.03}CoGe$

This material is available free of charge via the Internet at http://pubs.acs.org.