Supporting Information

Negative thermal expansion in (Sc,Ti)Fe₂ induced by unconventional magnetovolume effect

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Experimental methods: The polycrystalline alloy samples of $(Sc_{1,x}Ti_x)Fe_2$ (x = 0, 0.45, 0.6, 1.0) were prepared with the constituent elements of better than 99.9% purity by an arc melting under high purity argon atmosphere. To ensure homogeneity, the button samples were turned over and melted for many times. After melting, the samples were wrapped by Mo foils, and then annealed in a vacuum-sealed quartz tube at 1273 K for 7 days. The linear thermal expansion $(\Delta l/l_0)$ was measured by a thermo-dilatometer (DIL 402 Expedis Select). The room temperature high-energy synchrotron XRD patterns and synchrotron X-ray total scatterings of pair distribution function (PDF) of $(Sc_{1,x}Ti_x)Fe_2$ were collected at the beamline 11-ID-C of APS, Argonne National Laboratory with X-ray wavelength of $\lambda = 0.1173$ Å. The PDF structure refinements were carried out using PDFgui. The temperature dependence of NPD data with $\lambda = 2.41$ Å was collected at the high-intensity diffractometer Wombat of the Australian Nuclear Science and Technology Organisation (ANSTO). Magnetism properties were measured by physical property measurement system (PPMS) of quantum design with the vibrating sample magnetometer (VSM). The structure refinements for all diffraction data were analyzed by FULLPROF software.

Computational method and model: All the calculations are carried out using first-principles method based on density functional theory (DFT) as implemented in the Cambridge Serial Total Energy Package (CASTEP) program code (1,2). The pseudopotentials are obtained using the Koelling-Harmon solver for Sc $(3s^23p^63d^1 4s^2)$, Ti $(3s^23p^63d^24s^2)$ and Fe $(3d^64s^2)$ outer shells. Exchange-correlation effects are described by the generalized gradient approximation with PBE functional.(*3*) The wave functions are expanded by the plane waves up to an energy cutoff of 500 eV. Integrals over the first Brillouin zone (BZ) are approximated by a Monkhorst–Pack Kpoint meshes of $13 \times 13 \times 9$. The unit cell of ScFe₂ contains four Sc atoms and 8 Fe atoms. For the Ti-substituted system of Sc_{0.75}Ti_{0.25}Fe₂, one of four Sc atoms is substituted by Ti. The total energy of the system is calculated with spin polarization and converged to 10^{-8} eV/Å.

Magnetic structure analysis: The temperature dependence of magnetic reflection (100) and (002) of x = 0.6 and 0.45 is shown in Figure S9. For both x = 0 and x = 0.45, the intensity of (002) reflection keeps constant, while that of the (100) reflection decreases upon heating, which means that the ferromagnetic component is only along the *c*-axis. For x = 0.6, upon heating the intensity of the (002) reflection decreases firstly and then keeps constant, while that of the (100) reflection increases firstly and then decreases. It means that the appearance of ferromagnetic component in the basal plane firstly, and then the ferromagnetic component gradually turns to the direction of *c*-axis. According to the variable temperature NPD patterns, the magnetic structure of (Sc,Ti)Fe₂ has been revealed. For x = 0, it has a simple ferromagnetic structure (FM1) below T_C with the Fe magnetic moment along the *c*-axis (Figure 3c). For x = 0.45, there are two ferromagnetic states with the different moments (FM1 and FM2), and the Fe magnetic moments are always along the *c*-axis. For x = 1.0, it is antiferromagnetic below T_N . The Fe(6h) atoms carry a moment, which are coupled ferromagnetically in the (001) layer and antiferromagnetically between the successive layers, while the Fe(2a) atoms have no magnetic

moment (Figure S10). For x = 0.6, it has a canting magnetic structure at low temperature (T < 125 K), and then the magnetic moments gradually turn to the *c*-axis with increasing temperature. At high temperatures, there are two ferromagnetic states with different moments FM1 (125 K < T < 205 K) and FM2 (205 K < T < 365 K), in which the Fe magnetic moments are along the *c*-axis.



Supplementary figures and tables:





Figure S2. Structure refinements of NPD patterns of (a) x = 0 at T = 10 K; (b) x = 0.45 at T = 10 K; (c) x = 0.6 at T = 5 K; (d) x = 1.0 at T = 10 K.

Materials Horizons



Figure S3. Temperature dependence of unit cell volume of TiFe₂.



Figure S4. Temperature dependence of linear thermal expansion $(\Delta l/l_0)$ of $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45, 0.6, and 1.0) determined by a thermo-dilatometer.



Figure S5. Temperature dependence of magnetization (*M*-*T*) at a magnetic field 1000 Oe for $TiFe_2$ (x = 1.0).



Figure S6. Temperature dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetization at a magnetic field 1 T for $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45, and 0.6).



Figure S7. Temperature dependence of magnetization (*M*-*T*) under different magnetic fields (0.01, 0.05, 0.1, 0.5, and 1 T) for $(\text{Sc}_{0.4}\text{Ti}_{0.6})\text{Fe}_2$.



Figure S8. High-intensity NPD patterns for $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45, 0.6, and 1.0) at 10 K.



Figure S9. Temperature dependence of intensity of the magnetic reflection (100) and (002) for x = 0.6 and 0.45.



Figure S10. Antiferromagnetic structure of TiFe₂.



Figure S11. Lattice parameters of $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45, and 0.6), which are extracted from the NPD data.



Figure S12. The distances of Fe-Fe in $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45 and 0.6), which are extracted from the NPD data.



Figure S13. The total ferromagnetic moments at Fe(2a) and Fe(6h) in $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45, and 0.6).



Figure S14. Temperature dependence of (a) the magnetic moments at Fe(2a) ($M_{\text{Fe}(2a)}$), and (b) the relative change of unit cell volume ($\Delta V/V$) in three representative compositions of x = 0 (PTE), x = 0.45 (ZTE), and x = 0.6 (NTE).



Figure S15. Temperature dependence of total magnetic moments for one chemical formula of $(Sc_{1-x}Ti_x)Fe_2$ (x = 0, 0.45, and 0.6) calculated by $3/2M_{Fe(6h)}+1/2M_{Fe(2a)}$, which are obtained from NPD.

Table S1. Comparison of lattice dimensions and energy from the DFT calculations for three magnetic states: ferromagnetic (FM), paramagnetic (PM), and nonmagnetic (NM).

Formular	Magnetic state	E(eV)	V(A³)
ScFe ₂	FM	-93.835	167.50
	PM	-92.941	162.96
	NM	-92.763	160.01
Sc _{0.75} Ti _{0.25} Fe ₂	FM	-95.443	164.30
	PM	-94.853	160.13
	NM	-94.423	156.25
Sc _{0.5} Ti _{0.5} Fe ₂	FM	-97.051	160.54
	PM	-96.453	155.88
	NM	-96.208	152.63

¹ S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne, First principles methods using CASTEP, *Zeitschrift für Kristallographie-Crystalline Mater*. 220, 567-570 (2005).

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