Artificially produced rare-earth free cosmic magnet

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Chemically ordered hard magnetic L₁₀−FeNi phase of higher grade than cosmic meteorites is produced artificially. Present alloy design shortens the formation time from hundreds of millions of years for natural meteorites to less than 300 hours. Electron diffraction detects four-fold 110 superlattice reflections and a high chemical order parameter (S ≥ 0.8) for the developed L₁₀−FeNi phase. The magnetic field of more than 3.5 kOe is required for the switching of magnetization. Experimental results along with computer simulation suggest that the ordered phase is formed due to three factors related to the amorphous state: high diffusion rates of the constituent elements at lower temperatures when crystallizing, a large driving force for precipitation of the L₁₀ phase, and the possible presence of L₁₀ clusters. Present results can resolve mineral exhaustion issues in the development of next-generation hard magnetic materials because the alloys are free from rare-earth elements, and the technique is well suited for mass production.

Iron meteorites with Widmannstaetten type of structure are mainly composed of iron and nickel. This structure is formed through an extremely slow cooling rate of about one Kelvin per million years in the universe¹. The Widmannstaetten structure observed in Octahedrite-type meteorites is peculiar, and results from the apparent phase separation of the α-phase (bcc-FeNi with a mineral name: kamacite) and γ-phase (fcc-FeNi: taenite) at the FeNi interface. The taenite phase lamellae observed in the meteorite have varying Ni concentration zones (28–50%)². Both the disordered fcc and ordered L₁₀ phases of Fe-Ni were detected. Interestingly, the L₁₀ FeNi phase, which is also known as tetrataenite is a hard magnetic with a high saturation magnetization (Mₛ ~ 1270 emu cm⁻³) and a large uniaxial magneto-crystalline anisotropy (K₁ ~ 1.3 × 10⁷ erg cm⁻³)³–⁵. The theoretical maximum magnetic energy product of L₁₀ FeNi (~42 MG Oe) is close to the best rare-earth-based hard magnets recently developed⁶.

Due to shortage of rare-earth elements, which are currently used to produce high-grade permanent magnets, magnets free of rare-earth elements must be developed (i.e., hard magnets based on L₁₀ FeNi). Practically, it is impossible to produce L₁₀ FeNi magnet similar to meteorites industrially because the order-disorder transition temperature of L₁₀ FeNi is too low 320 °C²,⁶. The diffusion coefficients of Fe and Ni are extremely low around this temperature, and in reality, no diffusion takes place, which is why the ordered L₁₀ FeNi phase requires billions of years to form in cosmic products (meteorites). Since the discovery of the L₁₀ FeNi phase in the 1960s, several attempts (which might trigger atomic migration) such as irradiation with high-energy beams⁷, a nanoparticle technique⁸, mechanical alloying⁹, thin films comprised of mono-layered atoms¹⁰, and high-pressure torsion technique¹¹ have been tried to artificially produce this phase. However, L₁₀ FeNi-based hard magnets with high degree of chemical order have yet to be produced.

It seems that the production of L₁₀ FeNi-based hard magnets via conventional material synthesis utilizing atomic diffusion in the crystalline state is extremely difficult, if not impossible. The high stability of crystalline phase and the extremely low diffusivity of the atoms around the order-disorder transition temperature (~320 °C) in crystalline alloys are the biggest hurdles. A high diffusivity of atoms at lower temperatures may successfully form the L₁₀ FeNi phase, but it is difficult to achieve. Although high-pressure torsion and high-energy ball-milling techniques can increase the diffusivity of atoms¹¹, the increase is

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insufficient. A high atomic diffusivity is possible at low temperatures, such as the transformation from an amorphous state to a stable crystalline state. Distribution of elements in the amorphous alloy is similar to the initial state of meteorites (chondrule). At the dawn of the universe, chondrules were formed by the condensation of solar nebula and melting of condensed mineral clumps. A liquid like state in an amorphous alloy (similar to chondrule) can exist at room temperature. The major difference in approaching a stable crystalline state from the amorphous state is the drastic increase in diffusivity at the transition temperature (i.e., crystallization temperature), whereas cooling molten alloys decreases the diffusivity at the transition temperature. If an alloy based on \(~Fe\) \(_{50}Ni\)\(_{50}\) can be made into an amorphous state with a crystallization temperature close to the order-disorder transition temperature, then \(L1_0\) FeNi-based magnets may be realized.

Results
Various Fe-based amorphous alloys have been developed\(^{12}\). Generally, the crystallization temperature of these alloys is much higher (>450°C) than the order-disorder transition temperature of the \(L1_0\) FeNi phase. Recently, we have developed new high magnetic flux density FeSiBPCu-based nanocrystalline soft magnetic alloys\(^{13,14}\). The initial state of the FeSiBPCu alloy is amorphous, but it crystallizes into nano-crystalline \(\alpha\)-Fe in the remaining amorphous matrix below 400°C. Crystallization of this amorphous alloy is very rapid (i.e., the atomic diffusivity of the constituent elements is very high)\(^{15}\). Additionally this alloy also contains Phosphorus (P), which is also present in the NWA 6259 meteorite\(^6\). These characteristics are very promising for developing \(L1_0\) FeNi-based hard magnets.

Therefore, we replaced Ni with Fe in the FeSiBPCu alloy. The results suggest that the Fe\(_{42}Ni\)\(_{41.3}Si\)\(_{8}B\)\(_{4}P\)\(_{4}Cu\)\(_{0.7}\) alloy is the best among the investigated compositions. It should be noted that we also investigated crystalline FeNi binary alloys, but the formation of \(L1_0\) FeNi could not be detected. In Fe\(_{42}Ni\)\(_{41.3}Si\)\(_{12}B\)\(_{x}\)\(_{4}P\)\(_{4}Cu\)\(_{0.7}\) (\(x\) = 2 to 8 at.%) alloys, a higher Si content is better for the formation of the \(L1_0\) FeNi phase.

The as-quenched state of the Fe\(_{42}Ni\)\(_{41.3}Si\)\(_{8}B\)\(_{4}P\)\(_{4}Cu\)\(_{0.7}\) alloy is amorphous and its crystallization temperature measured by differential scanning calorimetry (DSC) is ~400°C (at a heating rate of 40°C/minute). Figure 1 shows the X-ray diffraction (XRD) pattern of the Fe\(_{42}Ni\)\(_{41.3}Si\)\(_{8}B\)\(_{4}P\)\(_{4}Cu\)\(_{0.7}\) ribbon crystallized at 400°C for 288 hours. The diffraction peaks corresponding to the ordered \(L1_0\) FeNi phase (inset of Fig. 1) along with \(\alpha\)-Fe and Fe\(_3\)B phases are also detected.

Figure 2a shows a bright-field (BF) scanning transmission electron microscope (STEM) image of the Fe\(_{42}Ni\)\(_{41.3}Si\)\(_{8}B\)\(_{4}P\)\(_{4}Cu\)\(_{0.7}\) alloy after annealing at 400°C for 288 hours. The microstructure is composed of 30-50 nm sized polycrystalline grains. Elemental mapping by energy dispersive X-ray spectroscopy (EDX) using STEM reveals that these grains include at least three phases: an Fe-rich phase, a Ni-rich phase and a nearly equi-atomic Fe\(_{50}Ni\)\(_{50}\) alloy phase (Fig. 2b). It should be mentioned that Si and P were detected in the Ni-rich grains, but not in the Fe-rich or FeNi grains. Detection of Fe\(_3\)B phase by XRD indicates that B is distributed in Fe-rich phase. Areal fraction of these three phases are 40% (Ni-rich), 37% (Fe-rich), and 23% (Fe-Ni alloy). Thus, partitioning of the solute elements indicates that the Fe-rich
grains correspond to the $\alpha$-Fe and Fe$_3$B phases as detected by the X-ray measurements (Fig. 1). The Ni-rich grains are fcc, and the equi-atomic Fe$_{50}$Ni$_{50}$ regions are possibly made from L1$_0$ or fcc type of grains.

We obtained the nanobeam electron diffraction (NBD) patterns (probe size $\sim$0.5 nm), which include, the superlattice reflections from an area within the equi-atomic FeNi alloy phase. Figure 2c,d show the [001]-zone NBD patterns obtained by scanning a grain marked by an encircled region in Fig. 2a,b. The existence of four-fold 110 superlattice reflections clearly indicates that the L1$_0$-type ordered phase is formed with the c-axis oriented normal to the specimen plane. This is consistent with the XRD measurements. Volume fraction of the L1$_0$ phase is roughly estimated to be $\sim$8% based on the STEM-EDX elemental map together with NBD patterns by assuming a spatially random orientation of the c-axis.

The long-range order (LRO) parameter ($S$) is approximately $\sim$0.8 or above, which was estimated based on simulations of the NBD patterns as a function of LRO parameters. Surprisingly, this value is higher than that reported for natural meteorites ($S=0.608$)$^{16}$. It is possible that $S$ is reduced due to heating of a natural meteorite surface upon entering the Earth’s atmosphere.

Figure 2e shows the simulated NBD pattern of the L1$_0$-FeNi structure with $S=0.8$. Superlattice reflections are marked in red color. It should be mentioned that the polycrystalline nature may prevent frequent detection of the ordered structure; intensity of the superlattice reflection is sensitively degraded by misorientation from the exact zone axis. Additionally, the possible distribution of the degree of order cannot be detected; we found that the superlattice reflections are too weak, and practically invisible in simulations when $S$ is below 0.75. Regardless of the aforementioned effects, we have successfully detected the single crystal electron diffraction patterns as demonstrated in Fig. 2c,d. This is a strong experimental evidence for the L1$_0$ phase formation. Thus, the state-of-the-art electron imaging unveils the presence of the highly ordered L1$_0$ phase in annealed Fe$_{42}$Ni$_{41.3}$Si$_8$B$_4$P$_4$Cu$_{0.7}$ ribbons. Here, it is worth mentioning that such a high degree of chemical order and a clear presence of superlattice reflection for L1$_0$ FeNi have not been reported yet.

Figure 3a shows the temperature dependent magnetization curve for the Fe$_{42}$Ni$_{41.3}$Si$_8$B$_4$P$_4$Cu$_{0.7}$ alloy after annealing at 400°C for 288 hours. There are two magnetic phases with Curie temperatures $T_{c1} \sim 500$-550°C, and $T_{c2} \sim 700$-750°C. Based on our structural analysis and reported literature$^{17,18}$, the $T_{c1}$ could be for L1$_0$ FeNi or Fe$_3$B, and $T_{c2}$ for $\alpha$-Fe phases. Metalloid rich phases are believed to be non-magnetic at/above room temperature. Among all the magnetic phases present in the alloy, only L1$_0$ FeNi is hard magnetic. If it is so, the hysteresis curve can reveal the presence of soft and hard magnetic phases. Figure 3b shows the hysteresis curve measured by applying a maximum magnetic field of $\sim$12,000 Oe perpendicular to the ribbon plane. The saturation magnetization ($M_s$) and coercivity are $\sim$100 emu/g and 700 Oe, respectively. A rapid increase in the magnetization at a lower magnetic field and the linear variation at higher magnetic fields suggest two processes: (1) alignment of the out-of-plane magnetization at low fields by the domain wall motion and (2) rotation of the in-plane magnetization to the out-of-plane at
higher fields. The second process can be easily understood based on the presence of soft magnetic phases (α-Fe and Fe3B phases), which have magnetic easy axes in the ribbon plane.

The magnetic easy axis of L1₀ FeNi is along the c-axis, which is perpendicular to the ribbon plane (due to texture). It seems the alignment of the out-of-plane magnetization at a lower field by the domain wall motion is due to the presence of hard magnetic L1₀ FeNi grains whose c-axis is along the field direction. Since the sample is polycrystalline, grains with mutually orthogonal c-axis ie. along [100] and [010] can contribute to linear increase in magnetization at higher fields (in addition to soft magnetic α-Fe and Fe3B phases). Such a linear increase in magnetization was also observed for the meteorites. In the absence of a magnetic field, the magnetization of grains tends to remain along the easy axis of magnetization (i.e., out-of-plane for L1₀ FeNi and in-plane for the soft magnetic phases). Therefore, the remanent magnetization \( M_r \) in Fig. 3b is approximately due the L1₀ phase, but the \( H_c \) in the out-of-plane direction is strongly influenced by the rotation of the in-plane magnetization (higher the volume fraction of soft phase lower is the \( H_c \)). Low \( M_r \) (~10% of \( M_s \)) seems to be consistent with EDX elemental mapping, which suggest volume fraction of L1₀ phase is ~8%.

The magnetic reversal of L1₀ FeNi can be understood from the dc demagnetization remanent \( [M_s(H)] \) curve (Fig. 3b). Basically, \( M_s(H) \) is the remanent magnetization of the initially saturated L1₀ FeNi grains upon reversing the magnetic field. Figure 3b shows that a magnetic field of at least ~3.5 kOe is required to switch the magnetization of the L1₀ FeNi grains in the present alloy. It should be noted that the L1₀ FeNi grains oriented in other directions, and strong demagnetizing effect resulting from high \( M_s \) of α-Fe grains can assist in magnetization switching at lower magnetic fields. We believe the magnetization switching field of the present L1₀ FeNi grains is higher than 3.5 kOe, and it can increase further by increasing the volume fraction. Nevertheless, such a high switching field is consistent with the highly anisotropic nature of the L1₀ FeNi phase.

The magnetic domains were also imaged using magnetic force microscopy (MFM). A typical MFM image along with the surface topography is shown in the inset of Fig. 3b. To eliminate surface topography effects in the MFM image, the distance between the tip and the sample surface was varied from 25 nm to 100 nm. In all the cases, MFM images show the same features, suggesting that the image contrast mainly originates from the interaction of the magnetic tip with the out-of-plane magnetization of the sample. The magnetic domain patterns of the sample (shown in the inset of Fig. 3b) are similar...
to other hard magnetic nano-composites with soft and hard magnetic phases. Both the structural and magnetic characterizations confirm that the highly ordered L1₀ FeNi phase is formed artificially in Fe₄₂Ni₄₁.₃Si₈B₄P₄Cu₀.₇ ribbon crystallized at 400 °C for 288 hours. Although, the annealing temperature (~400 °C) for formation of ordered phase is higher than the order-disorder transition temperature (320 °C), our measurements Fig. 3a show onset temperature for disordering is ~530 °C. The results obtained are very similar to NW A 6259 meteorite.

Molecular dynamic (MD) simulations were performed to understand the phase stability (energy level). The Hamiltonians (H’s) for amorphous, bcc, fcc, and L1₀ phases are –384.6, –393.3, –396.7, and –397.2 kJmol⁻¹, respectively. According to H, the L1₀ phase is the most stable phase, and the other phases are energetically destabilized in the sequence of bcc, fcc, and amorphous. The G was also calculated for the amorphous (–20.9 kJmol⁻¹), bcc (–24.6 kJmol⁻¹), and fcc (–29.9 kJmol⁻¹) phases based on the CALPHAD method. Although we were unable to evaluate G for the L1₀ phase, it is estimated to be ~35 kJmol⁻¹ by referring to more accurate calculations for the formation enthalpy of the L1₀ phase based on CALPHAD and ab initio methods.

Figure 4 schematically diagrams the above thermodynamic results. The binary phase diagram of Fe–Ni Fig. 4a calculated using the widely accepted SSOL5 database demonstrates that Fe₅₀Ni₅₀ (at.%) is thermodynamically stable as a single fcc phase at T = 673 K (as drawn with both arrows). Analysis of G Fig. 4b also indicates a single fcc phase, and Fe₅₀Ni₅₀ is the composition at the edge of the phase separation between bcc (Symbol E in Fig. 4b) and fcc (a composition close to Symbol C marked with open circle in Fig. 4b).

Thermodynamic analysis can be used to roughly estimate the volume fraction of L1₀ FeNi phase in Fe₄₂Ni₄₁.₃Si₈B₄P₄Cu₀.₇ alloy. Calculations were performed with Thermo-Calc by using TCFE7 database for Fe-based alloys and steels. As a result, the volume fraction of fcc Fe₅₀Ni₅₀Si₁₀ phase, which is an equilibrium phase at T = 673 K in Fe₄₂Ni₄₁.₃Si₈B₄P₄Cu₀.₇ alloy is evaluated to be 77.6%. Therefore, by assuming G = –35 kJmol⁻¹ for L1₀ Fe₅₀Ni₅₀ phase, we estimated the G for Fe₅₀Ni₅₀Fe₅₀₋ₓ/₂Ni₅₀₋ₓ/₂Si₁₀ system with different Si contents (Fig. 4d). Thermodynamically, it is possible to decompose Fe₄₂Ni₄₁.₃Si₁₀ into Fe₅₀Ni₅₀ and Fe₉₈Ni₈₈Si₁₂. Based on lever
rule (as indicated by red arrow in Fig. 4d), volume fraction of $\text{L1}_0 \text{FeNi}$ phase was estimated as $\sim 1/6$th of 0.776 i.e. $\sim 13\%$. This is close to the experimental value of $\sim 8 \text{ to } 10\%$.

We believe that the formation of the ordered phase is due to simultaneously achieving three factors; 1. High diffusion rates of the constituent elements at lower temperatures when crystallizing from an amorphous phase, 2. A large driving force for precipitation of the $\text{L1}_0$ phase from the amorphous state, and 3. Presence of compositional and structural fluctuations in the heterogeneous amorphous structure (similar to amorphous FeSiBPCu alloys$^{14,15}$), which play a role of the nuclei (clusters) when forming the $\text{L1}_0$ phase.

Although, the volume fraction of $\text{L1}_0 \text{FeNi}$ phase is low ($\sim 8 \text{ to } 13\%$), the hard magnetic $\text{L1}_0$ phase developed in the present study is both academically and industrially novel. First, the melt-spinning technique, and low temperature annealing are able to produce the $\text{L1}_0 \text{FeNi}$ phase at a much faster rate than the natural process (millions of years are required for meteorites). Second, the artificial $\text{L1}_0$ phase has a much higher chemical order than natural meteorites. Third, the non-equilibrium processing technique provides a new method to create a low temperature phase (such as $\text{L1}_0 \text{FeNi}$), which is difficult to obtain using conventional processing. Here, it is also important to mention that the quasicrystals were first formed through non-equilibrium processing technique only, and later they were discovered even in meteorite$^{11}$. Fourth, the present results shed light on hard magnetic materials, which have been stagnating since the discovery of rare-earth-based magnets almost 30 years ago. Fifth, thermodynamic analysis and non-equilibrium processing reported in this article should help in stimulating the research and development of new alloy systems with higher volume fractions of hard magnetic $\text{L1}_0 \text{FeNi}$ grains. Sixth, and most important, the realization of hard magnets free of rare-earth metals may help in resolving the global issues of resource exhaustion, which should become a critical in the near future. Hence, the successfull synthesis of the chemically ordered $\text{L1}_0 \text{FeNi}$ phase is one-step closer to the field of materials science for realizing a safe and sustainable society in the 21st century.

Methods

Experiments. Alloy ingots of $\text{Fe}_{80}\text{Ni}_{10}\text{Si}_{12}\text{P}_{12}\text{Cu}_{8-x}$ ($x = 2 \text{ to } 8 \text{at.\%}$) were made by high frequency melting. These alloy ingots were used to prepare ribbons via a single roller melt-spinning technique in air. Annealing was performed by sealing the ribbons in an Ar-gas filled silica tube, which was inserted in a furnace preheated to the required annealing temperature. A Rigaku (Smart Lab) X-ray diffractometer was used to identify the structure. Commercially available software (CrystalMaker) was used to fit the experimentally obtained X-ray diffraction curves. A vibrating sample magnetometer (VSM) was used to measure the saturation magnetization ($M_s$), coercivity ($H_c$), and dc remagnetization remanence [$M_R(H)$] curves. To measure $M_R(H)$ in the out-of-plane direction, the ribbon sample was exposed to a positive magnetic field of 10,000 Oe, which was applied normal to the ribbon plane. The field was made to zero and a remanent magnetization was recorded. Then a small negative magnetic field was applied and then switch to zero, and remanent magnetization was measured. Similar steps were repeated for the increasing negative magnetic field to obtain the $M_R(H)$ vs $H$ curve. Some of the annealed ribbons were thinned by Ar ion milling for electron transparency. Microstructures of the specimens were characterized using a JEOL JEM-ARM200F scanning transmission electron microscope (STEM) operating at 200 kV with a CEOS aberration (Cs) corrector for the probe-forming lens and a cold field emission gun (cold-FEG). Nanobeam electron diffraction patterns were obtained by a scanning fine electron probe (probe size $\sim 0.5 \text{ nm}$) with a beam convergence semi-angle of 3 mrad. Compositional analyses were carried out using an energy-dispersive X-ray spectrometer attached to the STEM. Specimen thickness was evaluated by electron energy-loss spectroscopy (EELS) in the STEM mode. The NBD patterns were simulated based on the Bloch wave calculation using the MacTempas software (Total Resolution LLC).

Simulations and calculations. Computational methodologies include molecular dynamics (MD) simulations and calculations of the phase diagrams and Gibbs free energy ($G$) based on equilibrium thermodynamics with targets of (a) amorphous, (b) $\text{bcc}$ (body-centered cubic), (c) $\text{fcc}$ (face-centered cubic), and (d) $\text{L1}_0$ phases using commercial software. The MD simulations were performed with Materials Explorer Version 5.0 (Fujitsu Production). For (a) amorphous, (c) $\text{fcc}$, and (d) $\text{L1}_0$ phases, 4,000 atoms comprised of 2,000 Fe and 2,000 Ni atoms were dealt with in the MD simulations, which corresponds to $10 \times 10 \times 10$ supercells in the conventional $\text{fcc}$ lattice where four atoms are accommodated in the unit cell. On the other hand, 3,456 atoms in total were dealt with for (b) $\text{bcc}$ phase, which corresponds to $12 \times 12 \times 12$ supercells in the conventional $\text{bcc}$ lattice with two atoms in the unit cell.

The following calculation conditions were applied to the MD simulations. The $\text{NTp}$ ensemble was selected to keep the number of atoms ($N$), temperature ($T$), and pressure ($p$) constant, where $p$ was set to atmospheric pressure (101.325 kPa). By an optimizing function in the software, the mass coefficient of a hypothetical heat bath in the Nosé scheme was initially determined to be 0.0643 for (a), (c), and (d) from the $\text{fcc}$ supercell and 0.0529 for (b) from the $\text{bcc}$ supercell. Un-distortable cubic lattices were used under GZ (Grujcic-Zhou)-type EAM (Embedded Atom Method) potentials with a cut-off distance of 1.02 nm (1.01 nm for (b)) and periodic boundary conditions. The aforementioned phases were created via the following procedure. (a) Amorphous phase was obtained by quenching at a cooling rate of $10^5 \text{ K/s}$ before and after holding the alloy for 2 ps at 1773 and 673 K, respectively. On the other hand, (b) $\text{bcc}$, (c) $\text{fcc}$, and (d) $\text{L1}_0$ phases were created by holding the initial states at 673 K for 2 ps. During the common
process at 673 K for 2 ps, we monitored the changes in the parameters, such as $T$, $p$, and lattice constants to avoid calculation errors (e.g., overshooting). Then each phase was further annealed at 673 K for 2 ps to evaluate the physical and thermodynamic values, such as density, lattice constants, as well as $T$, $p$, and volume as the primary monitoring variables.

The thermodynamic calculations and investigations were performed based on approaches from CALPHAD (CALculation of PHAse Diagrams) and SGTE (Scientific Group Thermodata Europe)\(^1\). Specifically, we utilized commercial software, Thermo-Calc version 4.1 (Thermo-Calc Software AB), with the SSOL5 database for solid solutions as well as TCFE7 database for Fe-based alloys and steels equipped in the software under atmospheric pressure.

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Acknowledgements

Part of the present study was supported by the “Tohoku Innovative Materials Technology Initiatives for Reconstruction (TIMT)”\(^2\) funded by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and the Reconstruction Agency of Japan, and a Grant-in-Aid for Challenging Exploratory Research (ID number of 30315642) from the Japan Society for the Promotion of Science (JSPS).

Author Contributions

A.M. oversaw the present study. Y.Z. fabricated the samples (master alloys and ribbons by melt-spinning) and carried out measurements (XRD, DSC, VSM) with K.T. under the direction of P.S. and A.M. P.S. was in charge of the analysis. K.S. carried out observations and structural analysis using TEM. A.T. performed the computational molecular dynamics simulations and thermodynamic calculations. All the authors (A.M., P.S., Y.Z., K.T., K.S. and A.T.) contributed to the discussion of the results. A.M., P.S., K.S. and A.T. wrote the manuscript.
Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Makino, A. et al. Artificially produced rare-earth free cosmic magnet. Sci. Rep. 5, 16627; doi: 10.1038/srep16627 (2015).

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