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Spin-glass behavior of Sn$_{0.9}$Fe$_{3.1}$N: An experimental and quantum-theoretical study

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Based on comprehensive experimental and quantum-theoretical investigations, we identify Sn$_{0.9}$Fe$_{3.1}$N as a canonical spin glass and the first ternary iron nitride with a frustrated spin ground state. Sn$_{0.9}$Fe$_{3.1}$N is the end member of the solid solution Sn$_x$Fe$_{4-x}$N (0 < x ≤ 0.9) derived from ferromagnetic γ'-Fe$_3$N. Within the solid solution, the gradual incorporation of tin is accompanied by a drastic weakening of the ferromagnetic interactions. To explore the dilution of the ferromagnetic coupling, the highly tin-substituted Sn$_{0.9}$Fe$_{3.1}$N has been magnetically reinvestigated. DC magnetometry reveals diverging susceptibilities for FC and ZFC measurements at low temperatures and an unsaturated hysteretic loop even at high magnetic fields. The temperature dependence of the real component of the AC susceptibility at different frequencies proves the spin-glass transition with the characteristic parameters $T_g$ = 12.83(6) K, $\tau^* = 10^{-11.8(2)}$ s, $\gamma^* = 5.6(1)$ and $\Delta T_g/(T_m\Delta \log \omega) = 0.015$. The time-dependent response of the magnetic spins to the external field has been studied by extracting the distribution function of relaxation times $g(\tau,T)$ up to $T_g$ from the complex plane of AC susceptibilities. The weakening of the ferromagnetic coupling by substituting tin into γ'-Fe$_3$N is explained by the Stoner criterion on the basis of electronic structure calculations and a quantum-theoretical bonding analysis. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4948984]

I. INTRODUCTION

The discovery of superconductivity in MgNi$_3$C\textsuperscript{1} has stimulated extensive research to study the physical properties of the transition-metal (M) based ternary nitrides AM$_3$N and carbides AM$_3$C with A being a metal element or a metalloid. Both nitrides and carbides adopt a simple antiperovskite-like structure in space group Pm$3m$ and feature remarkable properties, such as giant magnetoresistance effect (GMR),\textsuperscript{2-4} negative or zero thermal expansion (NTE or ZTE),\textsuperscript{5-7} nearly zero temperature coefficient of resistance (TCR),\textsuperscript{8,9} giant magnetostriction (MS),\textsuperscript{10} giant barocaloric effect,\textsuperscript{11} spin-glass behavior,\textsuperscript{12-19} and phase separation.\textsuperscript{20} These properties have been mostly found in Mn-based nitrides (AMn$_3$N)\textsuperscript{5-16} but recent investigations also focused on Ni-\textsuperscript{17} Co-\textsuperscript{17} and Cr-\textsuperscript{18} based antiperovskite nitrides (ANi$_3$N, ACo$_3$N, and ACr$_3$N). Surprisingly, similar properties have not been reported for ternary Fe nitrides (AFe$_3$N) even though the archetype γ'-Fe$_3$N with the same structure already exhibits exceptional magnetic properties, namely, a large saturation magnetization of 208 emu g$^{-1}$ and a low coercivity of $H_c$ = 5.8 Oe ≈ 460 A m$^{-1}$.\textsuperscript{21,22} Furthermore, γ'-Fe$_3$N shows high mechanical hardness and a large corrosion resistance.

Recently, we have studied the solid solution Sn$_x$Fe$_{4-x}$N (0 < x ≤ 0.9) showing drastic weakening of ferromagnetic interactions with increasing Sn concentration.\textsuperscript{23} The hypothetical upper limit of the solid solution, SnFe$_3$N, was theoretically modeled and evidenced important antiferromagnetic interactions. Such a weakening of ferromagnetic coupling can, combined with site disorder, give rise to magnetic frustration and result in a spin-glass behavior.\textsuperscript{24} By examining related chemical

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systems, a frustrated system was described for the amorphous binary alloy Fe\textsubscript{1−x}Sn\textsubscript{x}, where structural disorder comes together with site disorder.\textsuperscript{25} The magnetisms of Ga\textsubscript{0.9}Fe\textsubscript{3.1}N was analyzed by Mössbauer studies and understood as a kind of “cluster magnetism” where 13-atom Fe clusters are incorporated in a metallic gallium sublattice.\textsuperscript{26,27} Spin-glass behavior has only been found in several Mn-,\textsuperscript{12–16} Co-,\textsuperscript{17} Ni-,\textsuperscript{17} and Cr-based ternary nitrides. Up to the present day, however, there are no investigations of spin-glass behavior in A\textsubscript{x}Fe\textsubscript{4−x}N. The only known Fe-based spin glass is the carbide with the reported composition SnFe\textsubscript{3}C that exhibits a static glassy transition temperature of 20.3 K.\textsuperscript{19}

In the present study, a comprehensive magnetic characterization of Sn\textsubscript{0.9}Fe\textsubscript{3.1}N is carried out. We determine the equilibrium values of the magnetization by DC magnetometry, use AC measurements to gain insight into the magnetization dynamics, and describe the bonding situation on the basis of quantum-theoretical calculations.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Synthesis of Sn\textsubscript{0.9}Fe\textsubscript{3.1}N

Phase-pure, polycrystalline Sn\textsubscript{0.9}Fe\textsubscript{3.1}N was synthesized by a recently introduced two-step ammonolytic reaction\textsuperscript{23,28} starting from the powdered reactants Sn and Fe\textsubscript{2}O\textsubscript{3} that were mixed and finely ground using the 0.9:3.1 ratio of the metal atoms. This route avoids the formation of side products like ε-Fe\textsubscript{3}N\textsubscript{1+x}, intermetallic Fe–Sn compounds, binary iron nitrides, and elemental tin. The ammonolysis gas was a mixture of NH\textsubscript{3} (5.6 ml min\textsuperscript{−1}) and H\textsubscript{2} (8.4 ml min\textsuperscript{−1}). The following reaction conditions were used: 30 min at room temperature, 10 K min\textsuperscript{−1} to 210°C, 0.7 K min\textsuperscript{−1} to 250°C, 24 K min\textsuperscript{−1} to 1100°C, 2 h at 1100°C (sintering reaction), 17.3 K min\textsuperscript{−1} to 780°C, 5 h at 780°C (nitriding reaction), 24 K min\textsuperscript{−1} to room temperature; intensive grinding of the intermediate product; 10 K min\textsuperscript{−1} to 780°C, 10 h at 780°C (another nitriding reaction), 5 K min\textsuperscript{−1} to room temperature. For a detailed synthetic description and additional information on structure, composition, and magnetic properties see Ref. 23.

B. SQUID magnetometry

The DC susceptibility and the hysteretic loop were determined by SQUID magnetometry (Quantum Design MPMS-5XL). Field-cooled (FC) and zero-field-cooled (ZFC) DC magnetization curves were measured in the temperature range \(T = 2–350\) K at probing fields \(H = 100\) and 1000 Oe. In the FC measurement, magnetization data were collected while the sample was cooled down under the external field. In the ZFC measurement, the sample was first cooled down without an external magnetic field and the data were collected while warming up the sample with the probing field. The hysteretic loop was recorded at \(T = 5\) K within a field range \(B_0 = \pm 5\) T. The data were corrected for diamagnetic contributions of sample holder and compound.

C. ACMS measurements

Alternating current magnetic susceptibility measurements were performed with an AC magnetometry system (ACMS) at a Physical Property Measurement System (PPMS, Quantum Design). The measurements were carried out in the temperature range \(T = 5–30\) K at a small DC probing field of \(H_{DC} = 10\) Oe and a very small AC amplitude of \(h_{AC} = 10\) Oe after zero-field cooling the sample from room temperature. The magnetic susceptibility was measured by taking the derivative \(\partial M/\partial h\) at angular frequency \(\omega\) varying over a wide frequency range 100 \(\leq f \leq 10000\) Hz such as to cover a large time scale for studying the spin-glass dynamics.

D. Computational details

\(2 \times 2 \times 2\) supercells of \(A_x\text{Fe}_{4-x}N\) (\(A = \text{Fe}, \text{Sn}, \text{or both}\)) containing eight formula units were iterated towards self-consistency using the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{29–31} based
on density-functional theory (DFT). The projector-augmented-wave (PAW) potentials\textsuperscript{32,33} for core- and valence-electron separation were applied. Exchange and correlation contributions were treated with the generalized gradient approximation as parametrized by Perdew, Burke, and Ernzerhof (GGA-PBE).\textsuperscript{34} An $8 \times 8 \times 8$ Monkhorst-Pack\textsuperscript{35} $k$-point grid was used for Brillouin-zone integration. The kinetic energy-cutoff of the plane-wave expansion was 500 eV. Spin-polarized calculations were performed with integer starting values for all local magnetic moments, namely, 3 for all magnetically active elements and 0 for all other elements. Forces, stress tensors, atomic positions, unit cell shapes, and unit cell volumes of the crystal structures were allowed to relax during optimization. Because of the expected small energy differences, the convergence criterion for all electronic structures was set to $10^{-6}$ meV. The atom-projected density-of-states (pDOS) and the projected crystal orbital Hamilton populations (pCOHPs) were derived from the LOBSTER program suite 2.0.0 for electronic-structure reconstruction.\textsuperscript{36–39}

III. RESULTS AND DISCUSSIONS

Previously, we have studied the entire solid solution Sn$_{x}$Fe$_{4-x}$N ($0 < x \leq 0.9$) of which Sn$_{0.9}$Fe$_{3.1}$N is the end member.\textsuperscript{23} To shortly summarize the results, Sn$_{0.9}$Fe$_{3.1}$N was obtained as a phase-pure, polycrystalline powder with the antiperovskite-like structure in space group $Pm\bar{3}m$ (see Figure 1) as evidenced by powder X-ray diffraction using Mo K\textsubscript{α}$_{1}$ radiation. A Rietveld refinement of the powder pattern yielded the composition Sn$_{0.878(3)}$Fe$_{3.122(3)}$N$_{y}$ with the lattice parameter $a = 3.8818(1)$ Å and further showed that Sn exclusively occupies the unit-cell corners (Wyckoff position 1$\alpha$). This type of ordering was also confirmed by quantum-theoretical calculations. For the highly tin-substituted iron nitride Sn$_{0.783(3)}$Fe$_{3.217(4)}$N$_{0.95(3)}$, its composition was confirmed as Sn$_{0.78(3)}$Fe$_{3.22(4)}$N$_{0.95(3)}$ by prompt gamma-ray activation analysis (PGAA). Within experimental resolution there is no nitrogen deficiency that would influence the compounds’ magnetic coupling.

A. DC Magnetization

The temperature-dependent field-cooled (FC) and zero-field cooled (ZFC) molar DC susceptibilities and the corresponding inverse ZFC susceptibilities of Sn$_{0.9}$Fe$_{3.1}$N are shown in Figure 2. At sufficiently high temperatures, the inverse susceptibilities can be well described by the Curie-Weiss law. All fitted parameters are displayed in Table I. The courses of the ZFC susceptibilities indicate a macroscopic FM coupling between the Fe atoms since the paramagnetic Curie-Weiss temperature has a positive value of 14(4) K or 11(3) K depending on the probing field. Strictly speaking, the Curie-Weiss law is only valid for low probing fields owing to saturation effects, and we, therefore,
FIG. 2. FC and ZFC molar DC susceptibilities of Sn$_{0.9}$Fe$_{3.1}$N as a function of temperature under probing fields of (a) $H = 100$ Oe and (b) 1000 Oe. (c) Inverse ZFC molar DC susceptibilities at both applied fields and the best fit of the Curie-Weiss law.

consider the ZFC susceptibility at 100 Oe and its Curie-Weiss fit as the more precise data. Then, the Curie constant is $1.60(3) \cdot 10^{-4}$ K m$^3$ mol$^{-1}$ and the effective magnetic moment results in $10.1(1)$ $\mu_B$ per unit cell or $3.26(3)$ $\mu_B$ per Fe atom in Sn$_{0.9}$Fe$_{3.1}$N assuming the same magnetic moment for all Fe atoms. Note that this is only an approximation because the Fe atoms in $\gamma'$-Fe$_4$N differ, namely $3.0 \mu_B$ for Fe on the cube’s corners (1a) and $2.0 \mu_B$ for Fe on the cube’s faces (3c). However, the effective magnetic moment deduced from the DC susceptibility measurements exceeds those values.

The temperature dependence of the FC and ZFC susceptibilities at low temperatures is shown in Figures 2(a) and 2(b). We note that the susceptibilities diverge at low temperatures, namely, below a maximum at 13 K that is more pronounced for the lower probing field of 100 Oe. This divergence indicates a collective spin behavior, such as spin-glass behavior, mictomagnetism and superparamagnetism, among others. Below 13 K the FC susceptibility has a nearly constant value. The ZFC susceptibility, however, increases with increasing temperature until it converges with the FC susceptibility. We also note that these are characteristic features of a spin glass since the magnetic moments are figuratively frozen below the spin-freezing temperature in case of a FC measurement which results in a constant value for the susceptibility. In a ZFC measurement the energy supplied by increasing temperature allows to align the frozen clusters of magnetic moments with respect to the external field to eventually reach magnetic saturation. These magnetic clusters are orientated anisotropically and have, therefore, differently sized energy barriers for rotation. Also,

| Probing field $H_{DC}$ (Oe) | 100  | 1000 |
|----------------------------|------|------|
| Temperature range $\Delta T$ (K) | 220–350 | 150–350 |
| Paramagnetic Curie-Weiss temperature $\theta_P$ (K) | 14(4) | 11(3) |
| Curie constant C (K m$^3$ mol$^{-1}$) | $1.60(3) \cdot 10^{-4}$ | $1.32(2) \cdot 10^{-4}$ |
| Effective magnetic moment of Fe atoms per unit cell $\mu_{eff}$ ($\mu_B$) | 10.1(1) | 8.5(1) |
higher external magnetic fields overcome these energy barriers so that the FC and ZFC susceptibilities converge already at lower temperatures and the characteristic features of a spin glass in a susceptibility measurement can be suppressed.24

The SQUID magnetometer was also used to measure a hysteretic loop at 5 K (Figure 3) which is clearly lower than 13 K, the maximum-susceptibility temperature. The S-shape hysteretic loop has a small coercivity and reaches no saturation within the range of the applied field ($B_0 = \pm 5$ T). This behavior is also typical for a spin glass, since full saturation is never attained in these systems even at the lowest temperatures and highest magnetic fields. Spin glasses lack ferro- or antiferromagnetic long-range order, and the peculiar local anisotropy prevents the external field from fully aligning the frozen moments into its direction.24

B. AC Magnetization

To confirm the spin-glass behavior of Sn$_{0.9}$Fe$_{3.1}$N, dynamic (AC) magnetic measurements were performed. The static glassy transition temperature, $T_g$, can be accurately determined by the frequency dependence of the real AC susceptibility component.

The temperature dependence of the real component of the AC susceptibility $\chi'_m$ at frequencies from 100 Hz to 10 kHz is plotted in Figure 4. The maximum point in the DC magnetization appears as a sharp peak at around 13 K and shows a clear frequency dispersion which always accompanies a magnetic glassy transition. As the frequency increases, the temperature $T_m$ at the maximum of this...
peak shifts to higher values. Using this dependency, a fit to the critical power law

$$\tau = \tau^* \left( \frac{T_m}{T_g} - 1 \right)^{-\zeta v} \tag{1}$$

with $\tau = (2\pi f)^{-1}$ was performed (inset of Figure 4).\textsuperscript{24,41} The law is based on the theory of dynamical scaling near a phase transition and its fit evidences the spin-glass-like transition. The fit results in three parameters characterizing the spin glass, namely, the static glassy transition temperature $T_g = 12.83(6)$ K, the relaxation time of an individual particle moment $\tau^* = 10^{-11.8(2)}$ s, and the dynamic critical exponent $\zeta v = 5.6(1)$. $T_g$ corresponds to the DC (equilibrium) value. The relaxation time $\tau^*$ lies well in the characteristic range of $10^{-8}$–$10^{-12}$ s, as well as $\zeta v$ that varies between 4 and 12 for different canonical spin glasses.\textsuperscript{24,41} For comparison, the related spin glass SnFe$_3$C is characterized by a higher $T_g$ of 20.3 K, a slower $\tau^*$ of $10^{-10.6}$ s, and a higher $\zeta v$ of 9.4.\textsuperscript{19}

Magnetic glassy transitions are also quantitatively characterized by the frequency shift of the temperature $T_m$. This very shift is obtained from $(\Delta T_m/T_m)$ per decade of the angular frequency $\omega$ as $\Delta T_m/(T_m \cdot \Delta \omega)$.\textsuperscript{24} Using this equation we have estimated the frequency shift of Sn$_{0.9}$Fe$_{3.1}$N to be about 0.015, and it falls in the range of known canonical spin glasses (0.005–0.018) but is significantly lower than the frequency shift in semiconducting and insulating spin glasses (0.06–0.08) and superparamagnets (0.3).\textsuperscript{24}

All these experimental findings clearly indicate that the observed maximum in the real AC susceptibility component arises from the spin-glass freezing of the magnetic moments in the sample and that Sn$_{0.9}$Fe$_{3.1}$N is a canonical spin glass (with RKKY indirect-exchange interactions).

In a spin glass, the magnetic spins have a time-dependent response to the external field. Their dynamics is either characterized by a single relaxation time $\tau$ or a distribution of relaxation times $g(\tau)$ and to be studied in the complex plane of the susceptibilities $\chi_m'$ versus $\chi_m''$ using the phenomenological description of Cole and Cole (like the “Cole–Cole plot” in dielectric relaxation).\textsuperscript{42} Exemplarily at 5 K, the plot is shown in the inset of Figure 5. Clearly, the entire set of data points for frequencies from 100 Hz to 10 kHz does not follow a semicircle centered on the $\chi_m'$ axis as it would result from the Casimir–du Pré equations for a single $\tau$. Therefore, we must assume a rather broad distribution of relaxation times $g(\tau)$.\textsuperscript{24} To briefly review,\textsuperscript{24,43} the Casimir–du Pré equations

$$\chi' = \chi_s + \frac{\chi^0 - \chi_s}{1 + \omega^2 \tau^2} \tag{2'}$$

$$\chi'' = \omega \tau \left( \frac{\chi^0 - \chi_s}{1 + \omega^2 \tau^2} \right) \tag{2''}$$

FIG. 5. Inset: Cole–Cole plot of susceptibility $\chi''$ vs. $\chi'$ at 5 K. The grey line illustrates the fit of the data points at high frequencies assuming a Cole–Cole symmetric distribution $g(\ln \tau)$.\textsuperscript{44} The black line fits all data points with the large distribution of spin relaxation times that is shown in the main graph.
will be changed by introducing $g(\tau)$ to

$$\chi' = \chi_s + \int_{\tau_{\text{min}}}^{\tau_{\text{max}}} \frac{\chi_0(\tau) - \chi_s(\tau)}{1 + \omega^2 \tau^2} g(\tau) \, d\ln \tau$$

(3')

$$\chi'' = \int_{\tau_{\text{min}}}^{\tau_{\text{max}}} \frac{\omega \tau \chi_0(\tau) - \chi_s(\tau)}{1 + \omega^2 \tau^2} g(\tau) \, d\ln \tau.$$  

(3'"

The Cole–Cole formalism itself uses a distribution of relaxation times that is symmetric on the logarithmic time scale ($\ln \tau$) rather than on a linear one ($\tau$). It further introduces a parameter $\alpha$ characterizing the width of the distribution. The distribution $g(\ln \tau)$ around the average relaxation time $\tau_c$ is deduced from the Cole–Cole equation

$$\chi(\omega) = \chi_s + \frac{\chi_0 - \chi_s}{1 + (i\omega \tau_c)^{1-\alpha}}$$

(4)

and is

$$g(\ln \tau) = \frac{1}{2\pi} \cos [(1 - \alpha) \ln (\tau/\tau_c)] - \cos (\alpha \pi).$$

(5)

On the basis of the Cole–Cole equation (4), $\chi''_m$ can be expressed as a function of $\chi'_m$, thereby allowing a fit of the experimental data as circular arcs.\textsuperscript{42,44} The fit is shown in the inset in Figure 5 (grey line) and it clearly describes only the data points at high frequencies. There are other known distributions $g(\tau)$\textsuperscript{45} that all do not fit the dynamics in the spin glass Sn$_{0.9}$Fe$_{3.1}$N. In more detail, the analytical problem is that $g(\tau)$ cannot be deduced directly from the equations (3). We therefore described our data with a normalized sum of several distribution functions ($\sum g_i(\ln \tau)$). The procedure has been carried out in an iterative fashion to gradually determine a more accurate $g(\tau)$. The result of this iterative process for the data set at a temperature of 5 K is shown in Figure 5. The fit (black line) eventually describes all the data points even at low frequencies. The obtained relaxation-time spectrum is dominated by times between $10^{-5}$ and $10^{-4}$ s. This is a quite slow time scale and results from competing long-ranged interactions. Faster relaxation times are not observed but a very long-time tail exists. This wide range of relaxation times (up to infinity) is typical for canonical spin glasses and complicates the extraction of $g(\tau)$ which is only justified if decades of frequencies are measured.\textsuperscript{24}

Until now, we only looked at the frequency dependence of $\chi'_m$ and $\chi''_m$ at a temperature of 5 K, far below the spin-glass transition. The distribution of the relaxation time also depends on the temperature, however, and we extracted the function for all temperatures up to $T_g$ (Figure 6). For temperatures above $T_g$, $\chi''_m$ drops below the detection limit such that a fit was impossible. The $g(\tau,T)$ plot shows that a temperature increase narrows the distribution function so that the long-time tail vanishes. Further, the dominant time range between $10^{-5}$ and $10^{-4}$ s increases even more. This dynamic behavior is consistent with other canonical spin glasses.\textsuperscript{24}

In Sn$_{0.9}$Fe$_{3.1}$N, 10% of the $1a$ (= Sn) Wycko positions are occupied by Fe atoms, to be considered as embedded local magnetic moments in an otherwise non-magnetic primitive Sn sublattice.

![FIG. 6. Distribution of spin relaxation times for temperatures $5 \, \text{K} \leq T \leq 12.8 \, \text{K} = T_g$.](image)
These Fe(1\text{a}) impurities cause oscillating RKKY polarizations via the conduction electrons. Such long-ranged interactions fall off with $1/r^3$, are overlap-distance dependent and lead to FM and AFM spin alignments. The RKKY interactions together with the statistical site disorder on 1\text{a} result in the aforementioned frustrated spin ground state in Sn$_{0.9}$Fe$_{1.1}$N.

C. Electronic structure and bonding

To develop a deeper, more chemical understanding of the spin-glass behavior of Sn$_{0.9}$Fe$_{1.1}$N we refer to the entire solid solution Sn$_{x}$Fe$_{3-x}$N with the well-studied FM γ′-Fe$_3$N on the one side and SnFe$_3$N with dominating AFM interactions as modeled theoretically in Ref. 23 on the other side. Throughout the solid solution the FM coupling is drastically weakened while Fe is replaced. This effect has been observed once before in the Ga-substituted ternary nitride. All other known ternary nitrides with the composition AFe$_3$N with $A = \text{In, Rh, Pd}$, and quite a number of other transition metals are ferromagnetic with high $T_c$. To analyze this “dilution” of the magnetism, the Stoner criterion may be used because it explains the ferromagnetism of transition metals resulting from, first, a large electronic density-of-states at the Fermi level ($\epsilon_F$) and, second, the presence of strong exchange interactions.

To evaluate the first condition, the two series limits, γ′-Fe$_3$N and SnFe$_3$N, as well as the in-between composition Sn$_{0.5}$Fe$_{1.5}$N were considered. They differ in their crystal structure only by the occupation of the Wyckoff position 1\text{a} with Fe, Sn, or both, and these atoms are coordinated cuboctahedrally by other Fe atoms on the Wyckoff position 3\text{c} (Fe(3\text{c})). The number of states at the Fermi level $N(\epsilon_F)$ in total and for a single Fe(3\text{c}) in γ′-Fe$_3$N, Sn$_{0.5}$Fe$_{1.5}$N, and SnFe$_3$N were extracted from LOBSTER atom-projected density-of-states calculations by analyzing non-spin-polarized electronic structures. As shown in Table II, $N(\epsilon_F)$ in total decreases significantly as more Sn is incorporated. Also, $N(\epsilon_F)$ of a single Fe(3\text{c}) is lower in SnFe$_3$N than in FM γ′-Fe$_3$N and FM Sn$_{0.5}$Fe$_{1.5}$N. The observed decrease in $N(\epsilon_F)$ in total and of a single Fe(3\text{c}) supports the idea of a weakening of the ferromagnetism with an increase in the Sn concentration according to the first condition of the Stoner criterion. γ′-Fe$_3$N fulfills this first condition and is a typical ferromagnet, while SnFe$_3$N does not fulfill the conditions and is a spin glass with RKKY interactions.

The LOBSTER program suite was further used to evaluate and compare the chemical bonding in γ′-Fe$_3$N and SnFe$_3$N (whose composition is close to the experimentally studied Sn$_{0.9}$Fe$_{1.1}$N) for selected atom pairs by the projected crystal orbital Hamilton population (pCOHP) method. Since we deal with magnetic systems, we used spin-polarized calculations this time, more precisely an FM ordering for γ′-Fe$_3$N and both FM and AFM orderings for SnFe$_3$N to somehow model its frustrated spin ground state. The pCOHP curves are integrated (with a weighted scheme) up to the Fermi level to provide ICOHP data for selected bonds (Table III). For reasons of brevity only pCOHP curves of A (1\text{a})–Fe(3\text{c}) and Fe(3\text{c})–Fe(3\text{c}) are shown in Figure 7.

The pCOHP curves for Fe interactions to its atomic neighbors in FM γ′-Fe$_3$N, FM SnFe$_3$N, and AFM SnFe$_3$N (most favorable cell-type B′, see Ref. 23) show the well-known splitting of the majority (α) and minority (β) spin channels. The interactions are optimized in terms of bonding, i.e., large contributions of antibonding Fe–Fe interactions at the Fermi level as found in corresponding non-magnetic models (data not shown) are avoided or at least minimized. The major contributors to the structural stability are the Fe(3\text{c})–N(1\text{b}) bonds resulting in large (more negative = bonding) ICOHP values. In contrast, the rather long-ranged A (1\text{a})–N(1\text{b}) interaction are negligible since the atoms are not in the first coordination of each other and there are no direct bonds. An important role

| Compound          | $N(\epsilon_F)$ in total | $N(\epsilon_F)$ of Fe(3\text{c}) |
|-------------------|---------------------------|----------------------------------|
| γ′-Fe$_3$N        | 11.1                      | 2.16                             |
| Sn$_{0.5}$Fe$_{1.5}$N | 9.1                      | 2.15                             |
| SnFe$_3$N         | 4.7                       | 1.49                             |
TABLE III. Average ICOHP values from spin-polarized LOBSTER calculations for various interatomic contacts in $\gamma'$-Fe$_4$N and SnFe$_3$N.

| Compound     | Spin arrangement | Lattice parameter (Å) | ICOHP (eV/bond) |
|--------------|------------------|-----------------------|-----------------|
|              |                  |                       | $(1a)\text{–}Fe(3c)$ | Fe$(3c)$–Fe$(3c)$ | Fe$(3c)$–N$(1b)$ | $(1a)\text{–}N(1b)$ |
| $\gamma'$-Fe$_4$N | FM               | 3.7910                | −1.003          | −0.713           | −3.086          | −0.030          |
| SnFe$_3$N    | FM               | 3.8928                | −1.500          | −0.508           | −2.920          | −0.136          |
| SnFe$_3$N$^a$ | AFM-B$^*$        | 3.8584                | −1.673          | −0.478$^*$FM     | −3.033          | −0.134          |

$^a$The energetically most favorable AFM arrangement B$^*$ was used. For a detailed explanation see Ref. 23 and 27. Out of the 96 Fe$(3c)$–Fe$(3c)$ interactions in the $2\times2\times2$ supercell there are 32 ferromagnetic and 64 antiferromagnetic. In purely mathematical terms, an average ICOHP value would result in −0.529 eV/bond.

is played by the A $(1a)\text{–}Fe(3c)$ and Fe$(3c)$–Fe$(3c)$ bonds. In each compound, they are both of the same distance due to the symmetry, but the Fe$(1a)\text{–}Fe(3c)$ bond in $\gamma'$-Fe$_4$N and the Sn$(1a)\text{–}Fe(3c)$ bond in SnFe$_3$N are clearly stronger than the corresponding Fe$(3c)$–Fe$(3c)$ bonds. The change in the bonding strength of A $(1a)\text{–}Fe(3c)$ and Fe$(3c)$–Fe$(3c)$ when incorporating Sn into $\gamma'$-Fe$_4$N is remarkable. While in $\gamma'$-Fe$_4$N the Fe$(1a)\text{–}Fe(3c)$ bond is 41% stronger than the Fe$(3c)$–Fe$(3c)$ bond, the Sn$(1a)\text{–}Fe(3c)$ bonds are about three times as strong as the Fe$(3c)$–Fe$(3c)$ bonds in both FM and AFM-B$^*$ SnFe$_3$N. Even though the FM and AFM-B$^*$ spin arrangements in SnFe$_3$N are only approximations of the ground state, they result in similar values and seem to come very close to the frustrated spin system in which both interactions exist. From the bonding analysis we conclude that incorporating Sn into $\gamma'$-Fe$_4$N significantly changes the bonding situation for the $1a$ and $3c$ atoms but the qualitative trends remain and shall apply for the entire solid solution Sn$_x$Fe$_{4-x}$N.

![Projected COHP (pCOHP) curves](image-url) of the A $(1a)\text{–}Fe(3c)$ and Fe$(3c)$–Fe$(3c)$ interactions in FM $\gamma'$-Fe$_4$N, FM SnFe$_3$N, and AFM SnFe$_3$N (cell-type B$^*$) as obtained from LOBSTER calculations. In all the plots, bonding states go to the right and antibonding states go to the left.
Let us briefly evaluate the second condition of the Stoner criterion for itinerant ferromagnetism, namely, the presence of strong exchange interactions. In an article by Meinert\textsuperscript{31} the Fe–Fe exchange interactions in $\gamma'$-Fe$_4$N were calculated. He concluded that within the distance of one unit cell the direct interactions dominate and that at larger distances, RKKY-like interactions play an important role. Not surprisingly, he found that FM coupling dominates for $\gamma'$-Fe$_4$N. For example, the Fe(1a)–Fe(3c) interaction (a strong chemical bond) exhibits a strong FM coupling. If non-magnetic Sn is incorporated into $\gamma'$-Fe$_4$N, these strong Fe(1a)–Fe(3c) exchange interactions are diminished and the Stoner criterion is no longer fulfilled. Furthermore, it is also remarkable that not all interactions in $\gamma'$-Fe$_4$N are of ferromagnetic nature.\textsuperscript{51} If the structure is divided in four primitive Fe sublattices (one for Fe(1a) and three for Fe(3c)) the 3c intra-sublattice interactions sum up strongly antiferromagnetic while the 3c inter-sublattice interactions are moderately ferromagnetic. If we transfer these findings to the spin glass Sn$_{0.9}$Fe$_{3.1}$N where most of the Fe(1a) are substituted by non-magnetic Sn, the remaining Fe(3c) couple ferro- as well as antiferromagnetically and apparently do not yield an ordered spin alignment. The few Fe(1a) atoms have a strong direct exchange with the Fe(3c) atoms and form ferromagnetic 13-atom Fe clusters as observed from the positive Curie–Weiss temperature. The Fe(1a) atoms further induce each an oscillating RKKY polarization, and, as they are randomly disordered, support the long-ranged disorientation of Fe(3c) spins. With reference to Meinert’s results, we can therefore explain the experimentally found spin-glass behavior of Sn$_{0.9}$Fe$_{3.1}$N.

IV. CONCLUSIONS

The combined DC and AC magnetometry experimentally confirm a magnetically frustrated ground state and the spin-glass behavior of Sn$_{0.9}$Fe$_{3.1}$N, the first ternary spin-glass iron nitride. The DC susceptibility shows the typical divergence at low temperatures for FC and ZFC measurements, and the hysteretic loop remains unsaturated even at high magnetic fields. The temperature dependence of the real component of the AC susceptibility at different frequencies classifies Sn$_{0.9}$Fe$_{3.1}$N as a canonical spin glass ($T_g = 12.83(6)$ K, $\tau^* = 10^{-11.8(2)}$ s, $\Delta T = 5.6(1)$, $\Delta\omega (\Delta T \cdot \Delta\omega) = 0.015$) with RKKY indirect-exchange interactions. The dynamic response of the magnetic spins to the external field is expressed by the distribution function of relaxation times $g(\tau, T)$ which shows a dominant relaxation-time range between $10^{-5}$ and $10^{-4}$ s up to $T_g$ and a very long-time tail that narrows with increasing temperature.

The weakening of the ferromagnetic coupling through an increasing tin concentration can be explained by the Stoner criterion. This is mirrored by a decrease in the number of states at the Fermi level in total and for a single Fe(3c) atom. Furthermore, the chemical bond between atoms on Wyckoff positions 1a and 3c is far stronger than the bond between atoms on neighboring 3c positions, and these differences become more distinctive with increasing tin concentration. The reason for the spin-glass behavior is that ferromagnetic and antiferromagnetic exchange interactions play important roles of comparable size in the solid solution Sn$_{x}$Fe$_{4-x}$N.

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