Juliane Stahl, Vladimir Pomjakushin and Dirk Johrendt*

Ferromagnetism in $Fe_{3-x-y}Ni_xGeTe_2$

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Abstract: Polycrystalline samples of $Fe_{3-y}GeTe_2$ ($0.08 \le y \le 0.29$) and the solid solutions $Fe_{3-x-y}Ni_xGeTe_2$ ($0.24 \le x \le 1.32$; $0.14 \le y \le 0.41$) were synthesized at 898–973 K in a resistance furnace and characterized by X-ray and neutron powder diffraction with Rietveld analysis (Fe_3GeTe_2 type, $P6_3/mmc$, a = 402.665(3), c = 1632.820(14) pm for $x = 0$, $y = 0.08$). Fe_3Ge layers with planar FeGe hexagons and additional iron atoms above and below the rings are separated by double layers of tellurium atoms. Fe_3GeTe_2 is ferromagnetic below T_C = 230 K with magnetic moments aligned along the c axis. T_C depends on the iron content and decreases with increasing iron vacancies continuously to 153 K in $Fe_{2.71}GeTe_2$. Further reduction of T_C is possible by nickel substitution until magnetic ordering is nearly absent in $Fe_{1.33}Ni_{1.32}GeTe_2$. The suppression of the magnetic ordering is caused by random dilution of the magnetic iron atoms either by vacancies or by nonmagnetic nickel atoms.

Keywords: crystal structure; iron; magnetic properties; telluride.

1 Introduction

Metallic compounds with quasi two-dimensional crystal structures and itinerant magnetism attract considerable interest [1, 2]. In contrast to localized magnetism of unpaired electrons in 3*d* or 4*f* shells, itinerant magnetism is not an atomic phenomenon but caused by correlations between the conduction electrons. Magnetic fluctuations occurring in such itinerant magnetic systems are currently believed to be one key to unconventional superconductivity [3, 4]. Therefore the search for new materials with weak itinerant magnetism is well underway. A compound of recent awakening interest is the telluride Fe_3GeTe_2 which is metallic and ferromagnetic below T_C = 230 K with a relatively low saturation moment of 1.2 μ_B per iron atom [5]. Recent more detailed studies [6, 7] revealed strongly anisotropic ferromagnetism with moments aligned along the *c* axis as expected from the pronounced two-dimensional character of the crystal structure. Interestingly, the analogous nickel compound Ni_3GeTe_2 shows no magnetic ordering but is a Pauli paramagnetic metal [5]. In contrast to Fe_3GeTe_2, the nickel compound shows significant electron density in the van der Waals gap between the tellurium layers in the crystal structure. The partial occupancy of the additional site is accompanied by a nickel deficiency in the NiGe hexagons. Due to the differences in the magnetic behavior of the iron and nickel compounds interesting properties of the solid solutions $Fe_{3-x}Ni_xGeTe_2$ are conceivable. These could occur if magnetic fluctuations persist while the ordering is suppressed. Furthermore Fe_3GeTe_2 has a composition range according to $Fe_{3-y}GeTe_2$ which also affects the Curie temperature [8]. Here we study the crystal structures and magnetic properties of the iron-deficient compounds $Fe_{3-y}GeTe_2$ and the solid solutions $Fe_{3-x-y}Ni_xGeTe_2$.

2 Experimental section

Polycrystalline samples of $Fe_{3-y}GeTe_2$ with nominal y = 0, 0.2, 0.4 and $Fe_{3-x-y}Ni_xGeTe_2$ with nominal x = 0.25, 0.5, 0.75, 1.0, 1.5 and y = 0.1 were synthesized from Fe, Ni, Ge and Te powder in alumina crucibles sealed in silica ampoules under argon atmosphere. In a first step the stoichiometric mixture was heated up to 898 K at a rate of 100 K h^{-1} and kept at this temperature for 60 h. After cooling at a rate of 100 K h^{-1} or 200 K h^{-1} the samples were ground in a mortar and – except for $Fe_{3-y}GeTe_2$ with nominal y = 0.2 and 0.4 – sintered at 973 K for 60 h with a heating and cooling rate of 100 K h^{-1}, respectively. For nominal $Fe_{2.8}GeTe_2$ the sintering step was carried out like the first one.

X-ray powder diffraction analysis of the samples was performed on a STOE STADI P diffractometer using Mo$K_{\alpha 1}$ radiation. Rietveld refinements were done using the Topas program package [9]. Energy-dispersive spectroscopy measurements were performed on a ZEISS EVO-MA

***Corresponding author: Dirk Johrendt,** Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13, D-81377 München, Germany, e-mail: johrendt@lmu.de
Juliane Stahl: Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13, D-81377 München, Germany
Vladimir Pomjakushin: Laboratory for Neutron Scattering, Paul Scherrer Institute, Villingen, CH-5232, Switzerland

10 microscope. Data was collected using a BRUKER X-Flash 410-M detector and the software QUANTAX 200. Magnetic measurements of the powder samples were carried out with a Quantum Design SQUID-Magnetometer MPMS XL-5. Neutron powder diffraction analysis was realized at the Laboratory for Neutron Scattering and Imaging at the Paul Scherrer Institute (Villigen, Switzerland) with the High-Resolution Powder Diffractometer for Thermal Neutrons. Data was collected with a wavelength of 188.570 pm at 3–300 K. Data refinement was done with the JANA2006 program package [10].

3 Results and discussion

3.1 Crystal and magnetic structure

The crystallographic data obtained from Rietveld refinements of X-ray and neutron diffraction patterns are fully consistent with those given in refs. [5, 7]. Neutron patterns at 3 K and 300 K are shown in Fig. 1. Small impurities of $Fe_{2.25}Te_2$ (1.0 wt %) and Fe_3O_4 (0.8 wt %) are identified by

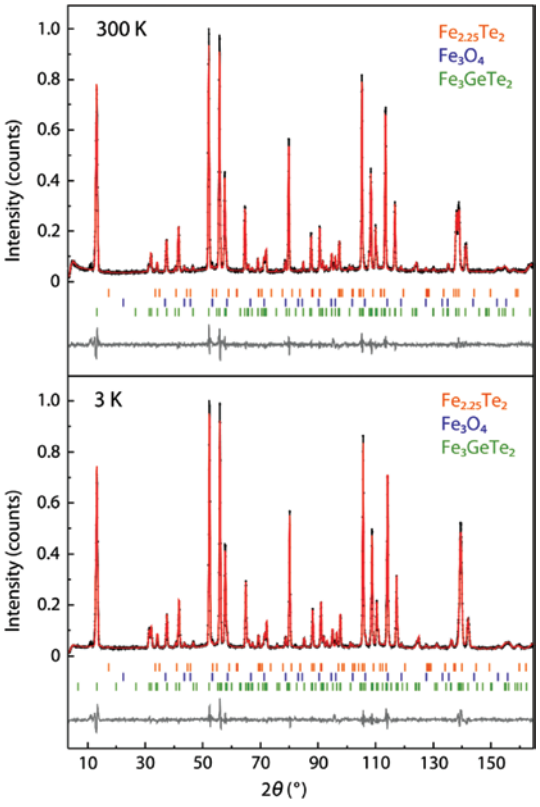

Fig. 1: Neutron diffraction patterns (λ = 188.57 pm) of Fe_3GeTe_2 at room temperature and at 3 K with Rietveld fits.

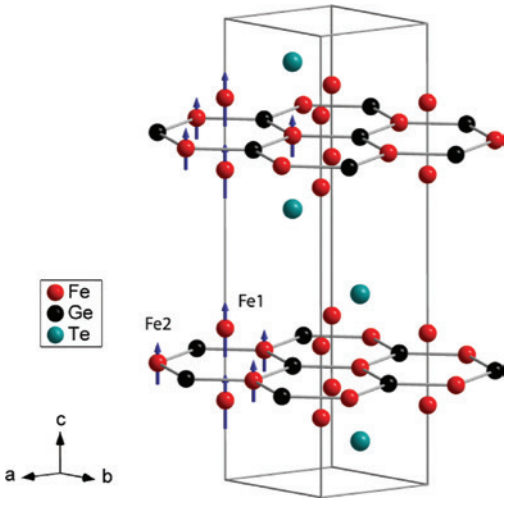

Fig. 2: Crystal structure of Fe_3GeTe_2 with magnetic moments ($\mu_{Fe1} = 1.75(6)\,\mu_B$, $\mu_{Fe2} = 1.07(16)\,\mu_B$) aligned ferromagnetically along the crystallographic *c* axis.

Rietveld analysis. Fe_3GeTe_2 crystallizes in the hexagonal space group $P6_3/mmc$ in its own structure type (Fig. 2), which contains Fe_3Ge layers similar to those present in Fe_2Ge [8, 9]. Fe_2Ge can be derived from the AlB_2-type structure with planar FeGe hexagons separated by additional iron atoms (Fe[FeGe]). Fe_2Ge is not stoichiometric but iron-deficient according to $Fe_{2-x}Ge$ ($x \approx 0.1$–0.5) with Fe vacancies on the Fe2 site in the FeGe hexagons as it is the case in $Fe_{3-y}GeTe_2$. The Fe_3Ge sheets are well separated by a double layers of tellurium atoms at an interlayer distance of 815 pm.

The compositions of the samples $Fe_{3-y}GeTe_2$ and $Fe_{3-x-y}Ni_xGeTe_2$ were determined by EDX measurements. Samples of $Fe_{3-y}GeTe_2$ are homogeneous up to $Fe_{2.7}GeTe_2$. The iron vacancies cause a shrinking of the unit cell volume through smaller lattice parameters *a* even though the *c* axis increases slightly (Table 1, Fig. 3). Further reduction of the iron content down to 1.33 is possible by substitution with nickel. The lattice parameters *a*, *c* and the cell volumes of the solid solution $Fe_{3-x-y}Ni_xGeTe_2$ decrease continuously but with smaller slopes than in $Fe_{3-y}GeTe_2$ because iron vacancies are now filled with nickel atoms. We point out that no nickel atoms are found in the van-der-Waals gap in our $Fe_{3-x-y}Ni_xGeTe_2$ samples up to $x = 1.32$, as it is the case for the pure nickel compound Ni_3GeTe_2 [5].

3.2 Magnetic properties

The top panel of Fig. 4 shows magnetic susceptibilities of $Fe_{3-y}GeTe_2$ and $Fe_{3-x-y}Ni_xGeTe_2$ measured from 300 to 2 K

Table 1: Lattice parameters *a* and *c*, unit cell volumes *V*, Curie temperatures T_C and saturation magnetizations μ^{sat} of $Fe_{3-y}GeTe_2$ and $Fe_{3-x-y}Ni_xGeTe_2$.

y (±0.05)	*x* (±0.05)	*a* (pm) (±0.07)	*c* (pm) (±0.3)	*V* (nm³) (±0.0005)	T_C (K) (±1)	μ^{sat} (μ_B) (±0.05 μ_B)
0.08	0	402.7	1632.8	0.2293	229	1.56
0.14	0	399.0	1636.0	0.2260	208	1.39
0.29	0	395.6	1639.5	0.2222	153	0.85
0.14	0.24	399.5	1630.9	0.2254	158	1.43
0.29	0.41	398.1	1629.6	0.2236	108	1.22
0.14	0.73	396.5	1627.4	0.2215	49	0.89
0.41	0.89	395.4	1625.2	0.2200	30	0.55
0.35	1.32	393.9	1620.2	0.2177	22	0.38
0.21	2.79	390.2	1602.2	0.2113	–	–

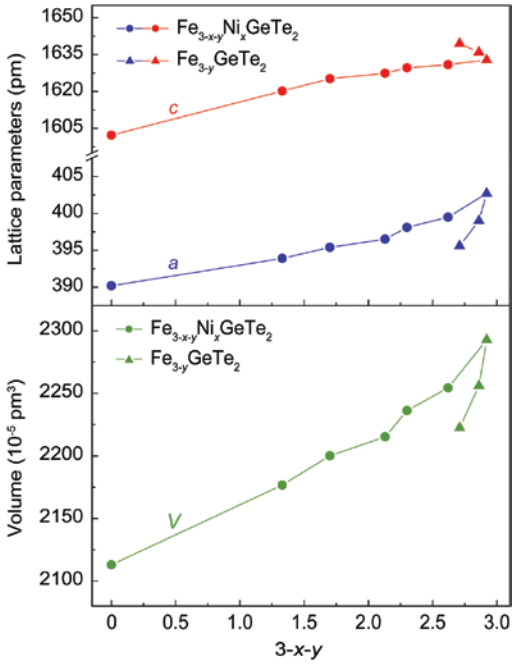

Fig. 3: Lattice parameters (top) and unit cell volumes (bottom) of $Fe_{3-y}GeTe_2$ and $Fe_{3-x-y}Ni_xGeTe_2$.

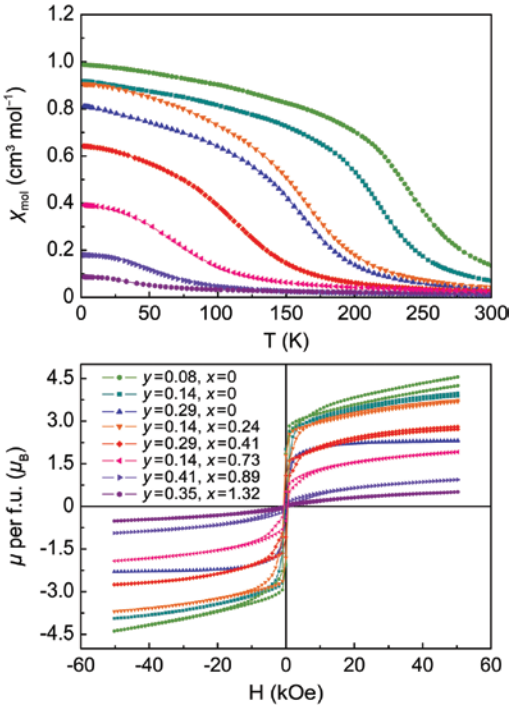

Fig. 4: Magnetic susceptibilities measured at 20 kOe (top) and isothermal magnetizations at 1.8 K (bottom) of $Fe_{3-y}GeTe_2$ and $Fe_{3-x-y}Ni_xGeTe_2$.

at 20 kOe external fields (1 kOe = 7.96×10^4 A m^{-1}). The zero points of the second derivatives $\left(\frac{d^2\chi}{dT^2}\right)$ reveal ferromagnetic Curie temperatures (T_C) which decrease continuously with the iron content from 229 K in $Fe_{2.92}GeTe_2$ down to 22 K in $Fe_{1.33}Ni_{1.32}GeTe_2$ (see Table 1). Thus magnetic ordering becomes successively suppressed as the iron vacancy concentration or the nickel content increases and is hardly detectable in $Fe_{1.33}Ni_{1.32}GeTe_2$. Isothermal magnetizations at 1.8 K confirm ferromagnetic ordering and the continuous decrease of the saturation moments from 1.56 μ_B in $Fe_{2.92}GeTe_2$ to 0.38 μ_B in $Fe_{1.33}Ni_{1.32}GeTe_2$ (Fig. 4 bottom). Coercive fields are small with values between 0.2 and 0.7 kOe which indicate that the materials are soft ferromagnets.

The ferromagnetism of these compounds in terms of T_C and μ^{sat} is not proportional to the valence electron count but depends on the iron concentration, as depicted in Fig. 5. Nickel remains non-magnetic as it is known from other nickel tellurides with layered structures which are exclusively Pauli paramagnetic metals [5, 10, 11]. The suppression of magnetic ordering turns out to be more efficient by introducing iron vacancies. However, this is only possible up to $Fe_{2.7}GeTe_2$ where the ferromagnetism is still present.

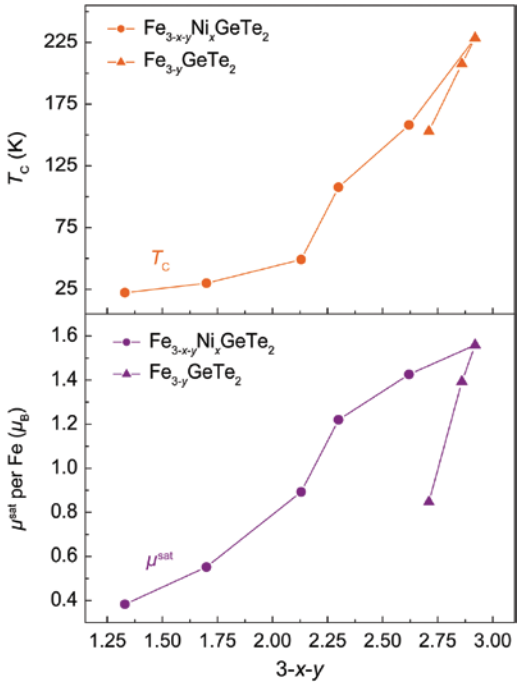

Fig. 5: Curie temperatures T_C (top) and saturation magnetizations μ^{sat} (bottom) of $Fe_{3-y}GeTe_2$ and $Fe_{3-x-y}Ni_xGeTe_2$ against the iron concentration.

4 Conclusion

Ferromagnetism in the compounds $Fe_{3-x-y}Ni_xGeTe_2$ is suppressed through random dilution of the magnetic iron atoms by either vacancies (most efficient) or by nonmagnetic nickel atoms. The Curie temperatures as well as the saturation moments decrease continuously as the magnetic coupling between the iron atoms becomes weaker. Similar suppression of magnetic ordering has also been observed in other layered tellurides, for example $Fe_{1.1-x}Ni_xTe$ (x = 0.02, 0.04, 0.08, 0.12) [12], as well as in the diluted antiferromagnet $Mn_xZn_{1-x}PS_3$ [13].

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