Crystal Growth of the Nowotny Chimney Ladder Phase Fe$_2$Ge$_3$: Exploring New Fe-Based Narrow-Gap Semiconductor with Promising Thermoelectric Performance

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Abstract

A new synthetic approach based on chemical transport reactions has been introduced to obtain the Nowotny chimney ladder phase Fe$_2$Ge$_3$ in the form of single crystals and polycrystalline powders. The single crystals possess the stoichiometric composition and the commensurate chimney ladder structure of the Ru$_2$Sn$_3$ type in contrast to the polycrystalline samples that are characterized by a complex microstructure. In compliance with the 18-$n$ electron counting rule formulated for T-E intermetallics, electronic structure calculations reveal a narrow-gap semiconducting behavior of Fe$_2$Ge$_3$ favorable for high thermoelectric performance. Measurements of transport and thermoelectric properties performed on the polycrystalline samples confirm the formation of a narrow band gap of $\sim$ 30 meV and reveal high absolute values of the Seebeck coefficient at elevated temperatures. Low glass-like thermal conductivity is observed in a wide temperature range that might be caused by the underlying complex microstructure.
Introduction

Intermetallic compounds formed in binary systems T-E, where T is a transition metal, and E is a p-metal or metalloid, are known as T-E intermetallics or polar intermetallics. In these compounds, the chemical bonding deviates significantly from the simple metallic bonding provoking extended interest and comprehensive studies. On one hand, peculiarities of the chemical bonding in T-E intermetallics provide a background for unusual physical properties, especially in the electronic transport, giving rise to narrow-gap semiconductors,\textsuperscript{1-6} high- and low-temperature thermoelectric materials\textsuperscript{7-11} as well as superconductors.\textsuperscript{12-14} This renders the T-E intermetallics promising functional materials for transport and thermoelectric applications. On the other hand, bonding between the T and E atoms in these compounds represents an intermediate case that can not be solely assigned to the limits of ionic, covalent or metallic bonding, thus markedly hindering its microscopic description and analysis. Recently, a unified picture of the chemical bonding in T-E intermetallics based on isolobal analogies to molecular T complexes began to take shape.\textsuperscript{15} A new approach, the 18-\textit{n} rule, has been formulated.\textsuperscript{16} It considers the formation of multicenter bonds between the T and E atoms as a pathway to achieve the 18-electron configuration for each T atom. Currently, this rule successfully explains the stability of more than 34 different classes of T-E intermetallic compounds.\textsuperscript{17}

The 18-\textit{n} rule goes back to the studies of crystal and electronic structures of the Nowotny chimney ladder phases (NCLs). NCLs are a class of T-E intermetallics with the general formula T\textsubscript{t}E\textsubscript{m} known for their unique structural flexibility. In the crystal structure, \textit{m}-step helices of E atoms are enclosed inside the 4-step helices of T atoms that form the tetragonal $\beta$-Sn-type arrangement. Helices of E atoms may be rather simple 2- or 3-step helices, or remarkably more complex ones leading to incommensurate modulations on top of the parent tetragonal structure. For NCLs, a set of empirical rules was established providing relations between stoichiometry, incommensurability of the crystal structure, and chemical bonding. According to the first rule,\textsuperscript{18} the total number of valence electrons per T atom in a NCL compound is
equal or almost equal to 14. The second rule accounts for the appearance of pseudoperiodicity in the crystal structure with a spacing that is directly related to the stoichiometry and real periodicity of the compound, \( c_{\text{pseudo}} = c/(2t-m) \).\(^{19}\) Electronic structure calculations elucidate the first electron-counting rule in terms of the opening of a pseudogap or a real gap in the vicinity of the Fermi energy providing for an additional stability of NCLs.\(^{18}\) Analysis of the band structure and chemical bonding reveals that such special electron count in the NCLs is connected with the formation of the 18-electron configuration of each T atom. Further, this rule was extended through the isolobal analogies to other intermetallic structure types leading to the more general 18-\( n \) rule.\(^{17}\) Hereby, the Nowotny chimney ladder phases are at the origin of our understanding of chemical bonding in the T-E intermetallics. Despite the recent progress in this field, the NCLs are still compounds that give rise to puzzling questions regarding their crystal and electronic structures.

Recently, a new NCL compound was discovered in the binary system Fe-Ge.\(^{20}\) This compound is thermodynamically stable only at relatively low temperatures below \( \text{ca.} \ 600 \ ^\circ\text{C} \) and remains hidden due to the kinetic inertness of iron and germanium at such temperatures. The \( \text{Fe}_2\text{Ge}_3 \) composition and \( \text{Ru}_2\text{Sn}_3 \) structure type were assumed by Gerasimov \textit{et al.} \(^{20}\) based on the data obtained for polycrystalline two-phase sample. However, neither the Rietveld refinement nor the proper indexing of the diffraction pattern was performed.\(^{20}\) Later, Li \textit{et al.} \(^{21}\) performed transmission electron microscopy study on a sample prepared under the same conditions and found indications of an incommensurately modulated Nowotny chimney ladder structure with the composition \( \text{FeGe}_\gamma \), deviating from the stoichiometric one with \( \gamma = 1.5 \). This incommensurability of the crystal structure presumably leads to a glass-like behavior characterized by the low thermal conductivity at high temperatures as proposed in a recent study by Sato \textit{et al.}, who established \( \text{FeGe}_\gamma \) as a promising thermoelectric material with the large power factor of 1.9 mW m\(^{-1}\) K\(^{-2}\) and the dimensionless figure-of-merit of 0.57 near 600 K.\(^{22}\)

Herein, we put forward a synthetic approach based on chemical transport reactions that enables us to overcome the kinetic passivity of Fe and Ge at low
temperatures and to obtain high-quality polycrystalline samples as well as single crystals of the Nowotny chimney ladder phase $\text{Fe}_2\text{Ge}_3$. We thoroughly investigate the crystal structure of this compound using single-crystal X-ray diffraction, powder X-ray diffraction, and transmission electron microscopy. First-principles electronic structure calculations provide insight into chemical bonding in this NCL compound. Transport properties measured on polycrystalline samples are discussed along with details of the electronic structure.
Experimental Section

Synthesis of polycrystalline samples of FeGe_γ was performed in two steps. First, Fe (powder, ≥ 99.99%, Sigma Aldrich) and Ge (chips, 99.999%, Sigma Aldrich) mixtures were prepared with a total mass of 0.5 g for the γ = 1.22; 1.35; 1.5; and 1.86 ratios that corresponds to 55; 57.5; 60 and 65 at.% Ge, respectively. The mixtures were placed inside quartz ampoules, which were evacuated to the residual pressure of 1×10^{-2} torr and sealed. The ampoules were annealed at 900 °C for 5 days in order to overcome the kinetic inertness of Fe and Ge through the use of high temperature. Then, the ampoules were cooled down to room temperature in the shut off furnace. The obtained mixtures were grinded and annealed again at 700 °C for 7 days. Phase analysis using powder X-ray diffraction (PXRD) technique shows that for each value of γ the mixture of FeGe (P6/mmm, CoSn-type) and FeGe_2 (I4/mcm, CuAl_2-type) is formed at the first step. Second, the pre-synthesized mixtures were placed into quartz ampoules together with 5 mg of I_2 crystals, which were purified by sublimation prior to the use. Ampoules were evacuated and sealed, annealed at 480 °C for 7 days, and cooled down to room temperature in the shut off furnace. After that, the samples were grinded again in an agate mortar, and subsequently annealed at 500 °C for another 7 days.

Growth of single crystals of Fe_2Ge_3 was performed using chemical-transport reactions. The pre-synthesized stoichiometric mixture of FeGe (P6/mmm, CoSn-type) and FeGe_2 (I4/mcm, CuAl_2-type) with a total mass of 0.5 g was loaded into a quartz ampoule together with I_2 and Mo(CO)_6 (1 and 3 mg·cm^{-3} per volume of the ampoule, respectively) as transport agents. The ampoule with length of 7 cm and inner diameter of 0.8 cm was sealed under the residual pressure of 1×10^{-2} torr, and annealed in a two-zone horizontal furnace having a temperature gradient along the tube. The starting mixture was placed at 480 °C, while the crystallization zone was kept at 450 °C for one week yielding a nonequilibrium mixture that contains well-shaped crystals of Fe_2Ge_3.

Characterization of samples was performed by the following techniques. The obtained powders and single crystals were analyzed using a scanning electron
microscope JSM JEOL 6490-LV equipped with energy-dispersive X-ray (EDX) analysis system INCA x-Sight. For quantitative analysis of the elemental composition, external standards provided by MAC Analytical Standards were used. Powder X-ray diffraction (PXRD) patterns were registered on a Bruker D8 Advance diffractometer (LynXEye detector, Cu source, no monochromator used, $\lambda = 1.5418 \, \text{Å}$). The sample with $\gamma = 1.50$ was measured with the use of monochromatic radiation (Ge monochromator, $\lambda = 1.540598 \, \text{Å}$). Single crystals were investigated using a Bruker D8 Venture single crystal X-ray diffractometer (PHOTON 100 CMOS detector, Mo source, graphite monochromator, $\lambda = 0.73071 \, \text{Å}$). The absorption correction was performed using the multi-scan routine (SADABS program). The crystal structure was solved by direct methods and subsequently refined against $|F^2|$ in the full-matrix anisotropic approximation using the SHELX-2016/6 program package. For the transmission electron microscopy (TEM) study, the powder samples were crushed, dissolved in ethanol and put on a Cu grid. The data were acquired on a Technai G2, on a Phillips CM 20, and on a FEI Titan aberration-corrected transmission electron microscope using double tilt holders. The HAADF-STEM simulation was performed using the MULTEM software package.

Electronic structure calculations were performed within the framework of density functional theory (DFT) using Full-Potential Local-Orbital minimum basis band-structure FPLO code (version 14.00-47). In the scalar relativistic regime, local density approximation (LDA) was used to treat the exchange-correlation energy. Integrations in the $k$-space were performed by an improved tetrahedron method on a grid of 24×24×24 $k$-points. Spin-polarized calculations were performed within the LSDA formalism on a grid of 12×12×12 $k$-points using the ferromagnetic and antiferromagnetic initial spin configurations. In the latter configuration, the Fe1 atom has a spin-up direction of moment, while the Fe2 and Fe3 atoms possess spin-down moments. All moments are aligned along the (001) direction of the unit cell.

Magnetic properties were measured on a collection of 11 single crystals of Fe$_2$Ge$_3$ with a total mass of 95(15) μg grown by chemical transport method. Magnetization was registered using a superconducting quantum interference device
(SQUID) magnetometer of the Magnetic Property Measurement System (MPMS 3, Quantum Design) at temperatures between 2 K and 300 K in external magnetic field of 7 T.

**Transport properties** were measured on pellets pressed from the FeGe\textsubscript{y} powder at external pressure of 100 bar at room temperature. In these conditions, the relative density of 85% has been achieved. Resistivity and thermoelectric properties were measured on rectangular-shaped pellets with typical dimensions of 0.8×0.3×0.2 cm\textsuperscript{3} using Resistivity and Thermal Transport options of the Physical Property Measurement System (PPMS, Quantum Design), respectively, at temperatures between 2 K and 400 K in zero magnetic field.
Results and Discussion

Chemical transport

Regarding the thermodynamic and kinetic properties of alloys in the Fe-Ge system, the existence of several binary phases, including $\beta$-phase, $\eta$-phase, Fe$_6$Ge$_5$, FeGe, and FeGe$_2$, is envisaged in the Ge-rich part of the phase diagram$^{29}$ (Figure 1). Kinetic properties play a central role in the system, since kinetic inertness of iron and germanium prevents the formation of compounds at temperatures below ca. 700 °C. Therefore, synthesis of the listed compounds requires activation of the iron-germanium interaction, and different routes can be employed for this purpose, among which thermal activation is the most commonly used. For instance, the mixture of Fe and Ge can be activated by sintering in a high-frequency furnace, by employing the arc-melting technique, or simply by annealing in the evacuated quartz ampoule at 1000 °C or higher.$^{30}$ Starting from the activated mixture, binary compounds can be synthesized, usually by the long-duration annealing of alloys at lower temperatures. The above synthetic approach based on thermal activation and post-annealing leads to the formation of thermodynamically stable compounds. Moreover, decomposition of such compounds, if allowed by phase relations, is usually hindered due to kinetic reasons, thus screening other binary compounds that are stable at low temperatures. The latter explains why the Fe$_2$Ge$_3$ phase, which is stable below 580 °C, remained undiscovered due to the high thermodynamic and kinetic stability of FeGe and FeGe$_2$. In fact, Fe$_2$Ge$_3$ can not be synthesized even by the long-duration annealing of the activated mixture of Fe and Ge below 580 °C, because the mixture is kinetically stable. Our results show that not even traces of the Fe$_2$Ge$_3$ phase could be detected in the synthesis products. Therefore, synthesis of Fe$_2$Ge$_3$ requires alternative routes that are applicable at temperatures below 580 °C.

Among such routes, the synthesis under pressure, activation by milling, or chemical transport reactions can be employed to enhance the iron-germanium interaction at low temperatures. Indeed, Gerasimov et al. obtained the new compound as a side product by employing the ball-milling procedure.$^{20}$ The authors conducted differential scanning calorimetry study on the FeGe$_2$ sample that was exposed to ball-
milling, and unexpectedly found two endothermic effects on the DSC curve at temperatures below 700 °C. They assigned the effect at 580 °C to the decomposition of a previously unknown phase that was roughly identified as "Fe$_2$Ge$_3$". According to Gerasimov et al., the Fe-Ge phase diagram additionally contains the Fe$_2$Ge$_3$ phase, which is stable at the temperatures below 580 °C, as shown in Figure 1. According to Li et al.,$^{21}$ the new phase Fe$_2$Ge$_3$ should rather be considered as FeGe$_{\gamma}$, implying the incommensurability of the crystal structure and possible off-stoichiometry ($\gamma \neq 1.5$). Hereafter, we will refer to the polycrystalline samples as FeGe$_{\gamma}$ and to the case of the ideal chimney ladder structure as Fe$_2$Ge$_3$, for clarity.

In addition to the mechanochemical synthesis,$^{20,21}$ Sato et al. introduced spark plasma sintering under pressure to obtain the bulk samples of FeGe$_{\gamma}$ with higher relative density.$^{22}$ Summarizing the synthetic aspects, we can underline that only mechanical activation was used previously to enhance the Fe-Ge interaction at low temperatures. This method of activation, combined with post annealing or spark plasma sintering at temperatures below 500 °C, leads to the formation of polycrystalline FeGe$_{\gamma}$ that was found to possess the complex, hitherto unsolved incommensurately modulated crystal structure. Difficulties in interpretation of the crystal structure of FeGe$_{\gamma}$ are also connected with the presence of admixtures, owing to the lack of precise control over the elemental composition of samples prepared by ball-milling and post-treatment. In order to improve the synthesis of FeGe$_{\gamma}$ and to obtain single crystals of the new compound, we introduced the chemical transport method that facilitates the Fe-Ge interaction at low temperatures.

We started with the thermal activation of the Fe-Ge mixtures using the standard ampoule technique. High-temperature annealing of the Fe-Ge samples with compositions in the range between 50 and 66.7 at.% Ge leads to the formation of FeGe ($P6_3/mmm$, CoSn-type) and FeGe$_2$ ($I4/mcm$, CuAl$_2$-type) according to the PXRD results. On the phase diagram (Figure 1), there are two phase fields adjacent to the desired Fe$_2$Ge$_3$ composition. The first field between 50 and 60 at.% Ge at temperatures below 580 °C corresponds to coexisting FeGe and Fe$_2$Ge$_3$, while the second field at temperatures below 530 °C with compositions from 60 up to 100 at.%
Ge is represented by the equilibrium mixture of Fe$_2$Ge$_3$ and Ge. The samples with $\gamma = 1.22$ and 1.35 fall into the first field, while the sample with $\gamma = 1.86$ is in the second field, and the stoichiometric composition $\gamma = 1.5$ is in between the two areas. According to the PXRD results, which are shown in Figure 2, the phase compositions of samples is in full agreement with the proposed phase relations. Indeed, the samples with $\gamma = 1.22$ and 1.35 contain the chimney ladder phase FeGe$_\gamma$ and FeGe ($P2_13$, FeSi-type). The amount of the latter increases with decreasing $\gamma$. At the same time, the sample with $\gamma = 1.86$ contains elemental germanium and FeGe$_\gamma$. It should be noted that peak positions of the FeGe$_\gamma$ phase slightly change with $\gamma$, indicating a narrow homogeneity range of the compound. The sample with the stoichiometric composition $\gamma = 1.5$ is represented primarily by the desired chimney ladder phase FeGe$_\gamma$ with minor amounts of the FeGe admixture ($P2_13$, FeSi-type). The appearance of a secondary phase in this sample again can be explained by a narrow homogeneity range for the FeGe$_\gamma$ phase.

The choice of iodine as transport agent is motivated by the following reasons. Iodine had been successfully used for preparation of different Fe-Ge compounds by the chemical transport method, because it reversibly forms volatile compounds with Fe and Ge. The following chemical transport reactions are proposed:

\[
3\text{Fe} + 4\text{I}_2 \leftrightarrow \text{Fe}_3\text{I}_8,
\]
\[
\text{Ge} + 2\text{I}_2 \leftrightarrow \text{GeI}_4.
\]

Note that Fe$_3$I$_8$ is only a conjectural product. It contains both the Fe(II) and Fe(III) species underlining that the formation of Fe(III) is responsible for the chemical transport of iron at temperatures below ca. 600 °C. The formation of Fe$_2$Ge$_3$ from the equimolar mixture of FeGe and FeGe$_2$ can be written as:

\[
3\text{FeGe} + 3\text{FeGe}_2 + 26\text{I}_2 \leftrightarrow 2\text{Fe}_3\text{I}_8 + 9\text{GeI}_4 \leftrightarrow 3\text{Fe}_2\text{Ge}_3 + 26\text{I}_2.
\]

Among the volatile products, GeI$_4$ has the highest equilibrium vapor-pressure at temperatures above 350 °C. At the same time, the volatility of Fe$_3$I$_8$ is not high at 400-500 °C. However, its partial pressure is high enough to initiate the chemical transport, and we found that the addition of iodine to the reaction mixture leads to the formation of the desired compound at 500 °C. The synthesis leads to polycrystalline
FeGe\(_\gamma\) with the size of crystallites typically in the range of 0.2-4 \(\mu\text{m}\). Presumably, nucleation is the rate-determining step of the process, and the formation of larger crystals is not observed in the reaction. Therefore, the chemical transport method with the choice of iodine as transport agent can be successfully utilized for the preparation of polycrystalline FeGe\(_\gamma\) on a par with the ball-milling technique. Moreover, the developed synthetic approach involves only the ampoule technique and does not require any special equipment, it is time-saving and easy to implement.

Furthermore, we continued developing the chemical transport method in order to obtain single crystals. To this end, we attempted experiments in the temperature gradient. However, we quickly realized that no transport occurs below 500 °C. Chemical transport in the temperature gradient 480-450 °C with the addition of iodine leads to the formation of a nonequilibrium mixture of the cubic FeGe (\(P2_1/3\), FeSi-type) and hexagonal FeGe (\(P6/mmm\), CoSn-type) in the heating zone, and elemental germanium in the crystallization zone. The formation of Ge among the products indicates that the partial vapor-pressure of the Fe-containing component is not sufficient. In order to improve the transport of Fe through the vapor phase, we chose Mo(CO)\(_6\) as an additional transport agent. Molybdenum hexacarbonyl Mo(CO)\(_6\) is a crystalline compound stable at room temperature that sublimates readily upon slight heating under vacuum. It decomposes according to the reaction Mo(CO)\(_6\) \(\rightarrow\) Mo(CO)\(_y\) + (6-\(y\))CO forming the nonvolatile Mo(CO)\(_y\) polymetallic clusters (\(y < 6\)) in the hot zone and providing the CO vapor for the chemical transport.\(^{32}\) The following chemical transport reactions may occur during the synthesis of Fe\(_2\)Ge\(_3\) with the use of I\(_2\) and Mo(CO)\(_6\) as transport agents:

\[
3\text{FeGe} + 3\text{FeGe}_2 + 15\text{CO} + 22\text{I}_2 \leftrightarrow \text{Fe}_3\text{I}_8 + 3\text{Fe(CO)}_5 + 9\text{GeI}_4 \leftrightarrow 3\text{Fe}_2\text{Ge}_3 + 15\text{CO} + 22\text{I}_2.
\]

The use of I\(_2\) together with Mo(CO)\(_6\) led to appearance of new single crystals with typical sizes in the range of 100-750 \(\mu\text{m}\) in the crystallization zone. According to the EDXS results, these crystals contain 40.2(7) at.% Fe and 59.8(8) at.% Ge close to the stoichiometric composition FeGe\(_\gamma\) with \(\gamma = 1.5\). Further, single-crystal XRD
experiments revealed the chimney ladder structure confirming that the desired compound was obtained.

Summarizing all of the above, the method of chemical transport can be efficiently employed to obtain polycrystalline samples of FeGe$_{\gamma}$ at the isothermal conditions with the use of iodine as transport agent. In this case, chemical transport reactions activate decomposition of FeGe$_2$ and FeGe, and facilitate the Fe-Ge interaction, thus eliminating kinetic barriers in the Fe-Ge system. In the temperature gradient with concomitant application of I$_2$ and Mo(CO)$_6$ as transport agents, single crystals can be obtained.

**Crystal structure: polycrystals**

The PXRD pattern of FeGe$_{\gamma}$ for $\gamma = 1.5$ presented in Figure 2 can not be indexed neither in the primitive tetragonal lattice that is expected for the Ru$_2$Sn$_3$-type of crystal structure$^{33}$ nor in the orthorhombic system expected for the Ru$_2$Ge$_3$-type chimney ladder phase.$^{34}$ Moreover, the observed reflections are shifted from the positions calculated for the idealized structure in a complex manner implying possible incommensurability, necessitating a TEM investigation of the polycrystalline samples of FeGe$_{\gamma}$.

According to the TEM results, an orthorhombic commensurate structure with cell parameters approximately $a \approx 5.45$ Å, $b \approx 5.6$ Å, and $c \approx 8.95$ Å is present in the sample. Representative selected area electron diffraction (SAED) patterns of this phase along the main zone axes are shown in Figure 3. Tilt series collected from different crystals allow to derive the reflection conditions $0kl$: $l = 2n$; $h0l$: $l = 2n$; $00l$: $l = 2n$; and $hkl$, $hk0$, $h00$, and $0k0$: no conditions, which indicates extinction symbol $Pcc$- and allows two orthorhombic space groups, $Pcc2$ and $Pccm$. From SAED patterns alone, differentiation between these groups is not possible.

Further investigations show that the phase with the incommensurate structure is also present in the sample. The SAED patterns taken along the [1-10] and [100] directions (Figure 4a and 4b) can be indexed with cell parameters approximately $a \approx 5.6$ Å, $c \approx 4.6$ Å, and $q = 0.49(3)$ $c^*$. With this $q$-vector, the [001] SAED patterns are indistinguishable from those of the commensurate phase (Figure 3c), because of the
absence of nonzero components along \( a^* \) and \( b^* \). However, also slightly different \( q \)-vectors were found, as shown in Figure 4c and the bottom inset in Figure 4a, where the components along \( a^* \) and \( b^* \) differ from zero. The patterns in Figure 4a and 4b with \( q = 0.49(3) \) \( c^* \) are similar to those in Ref. [21], and are in agreement with the reflection conditions of the superspace group \( I4_1/amd:00ss \) proposed in literature for incommensurately modulated NCLs,\(^{35}\) i.e. \( hklm: h + k + l = 2n, 0klm: m = 2n, 00lm: l + 2m = 4n, hhlm: 2h + l = 4n, \) and \( hk00: h = 2n \).

The commensurate and incommensurate phases are present as domains next to each other. This can be seen from the occurrence in the top inset of Figure 4a of the reflections at the centre of some pairs of satellites, which originate from domains of the commensurate phase.

In the earlier mentioned domains, where the \( q \)-vector has nonzero \( a^* \) and \( b^* \) components, the tetragonal symmetry is necessarily broken.\(^{36-40}\) The tetragonal model deduced below for the single crystals was used for generating the calculated image shown as an inset in Figure 4e. It shows a good agreement for the basic feature seen in the image. However, small deviations for the atomic positions are present, which can be explained using the incommensurate model elaborated by Ye et al. for the NCL compound \( \text{MnSi}_{2-x} \).\(^{40}\) According to Ye et al., the "orientation anomaly" is caused by systematic shifting of the helical arrangement of the metalloid atoms along the "chimney" in the transition metal sublattice. This effect can effectively be observed in the HAADF-STEM image in Figure 4d indicated by the white lines. The local variations in the \( q \)-vector are most likely due to local differences in chemical composition.\(^{21,41}\) Using the formula proposed in Ref. [21], \( \text{Ge/Fe} = 2 - c^*_{\text{Ge}}/c^*_{\text{Fe}} \), results in a composition \( \text{FeGe}_{1.51(3)} \) for \( q = 0.49(3) \) \( c^* \). Such deviations from the stoichiometric composition with \( \gamma = 1.5 \) are unfortunately too small to confirm with EDX analysis, as they are beyond the precision of EDX on a TEM instrument. In summary, two main phases appear in the polycrystalline sample of \( \text{FeGe}_\gamma \) (\( \gamma \approx 1.5 \)): (i) an orthorhombic commensurate structure with cell parameters \( a \approx 5.45 \text{ Å}, b \approx 5.6 \text{ Å}, \) and \( c \approx 8.95 \text{ Å} \) and space group \( Pcc2 \) or \( Pccm \); and (ii) an incommensurate phase that can be indexed with the superspace group used in literature for NCLs\(^{35,36}\),
i.e. \textit{I4}_1/\textit{amd}:00ss, and with approximate cell parameters $a \approx 5.55$ Å, $c \approx 4.55$ Å, and variable $q$, most frequently $q = 0.49(3)$ $c^*$. The patterns agree with the patterns characteristic of NCLs, however, the simultaneous presence of a commensurate and several slightly different incommensurate phases, and minor amounts of admixtures hinder fitting of the PXRD pattern of FeGe$_\gamma$ for $\gamma = 1.5$.

**Crystal structure: single crystals**

In the single-crystal X-ray experiments, the reciprocal space was carefully scanned in a search for the presence of superstructure reflections that would signify incommensurate modulation of the crystal structure. However, only reflections belonging to the undistorted conventional tetragonal unit cell were found. The data collected can be indexed in the primitive tetragonal unit cell with $a = 5.5848(8)$ Å and $c = 8.9400(18)$ Å. The $P-4c2$ space group (No. 116) was chosen on the basis of diffraction pattern symmetry and systematic extinction conditions. The crystal structure was solved by direct methods and refined against $|F^2|$. Details of the data collection at 100 K and structure refinement parameters are listed in Table 1, the atomic coordinates and selected interatomic distances are given in Tables 2 and 3, respectively.

Crystal structure solution and refinement show that the selected single crystals possess a normal commensurate chimney ladder structure. They are characterized by the stoichiometric composition Fe$_2$Ge$_3$, in contrast to polycrystalline FeGe$_\gamma$. Here, substantial difference between single-crystal and polycrystalline specimens appears, since the single crystals grown by chemical transport method do not show any indications of a crystal structure distortion or incommensurability that are observed in the case of polycrystalline FeGe$_\gamma$. Supposedly, it is the small size of crystallites that is responsible for the incommensurability, since small crystallites contain large amounts of imperfections in the crystal lattice, such as vacancies and dislocations, which are favorable for shifts of atoms from their ideal positions. In the case of single crystals rather the regular crystal structure is observed, in which a perfect match between the Fe and Ge sublattices yields non-distorted periodicity within a conventional unit cell of the Ru$_2$Sn$_3$-type.
A view of the crystal structure along the [001] and [100] directions is shown in Figure 5a. The crystal structure possesses the common feature of NCLs with Fe atoms forming the $\beta$-Sn-type arrangement of the condensed four-step helices aligned in the [001] direction. At the same time, Ge atoms are located within these helices of Fe atoms in the form of 3-step helices. The Fe and Ge atoms are arranged in a seemingly simple and rational way forming helices inside other helices. However, the coordination polyhedra of Fe atoms are rather complex. They can not be described in a simple way by comparing with conventional types of polyhedra. The coordination polyhedra of Fe atoms are presented in Figure 5b. Iron atoms in the Fe1 position have 6 short distances to the Ge atoms (Table 3) and are additionally connected via $\sim 3.0$ Å contacts to 2 Ge atoms and 4 Fe atoms, such that the coordination number of Fe1 increases from 6 to 12, when longer distances are considered. Similarly, each of the Fe2 and Fe3 atoms, in addition to the short Fe-Ge distances, possesses 4 other contacts of $\sim 3.0$ Å to Fe atoms. Thus, the Fe2 and Fe3 atoms can be assigned the coordination numbers of 10 and 12, respectively. The additional Fe-Fe contacts are from the Fe atoms within the 4-step helices of the $\beta$-Sn-type arrangement. Each Fe atom is connected with 4 other Fe atoms located at the distance of $\sim 3.0$ Å, and these Fe-Fe contacts are important when applying the modified 18-$n$ rule to Fe$_2$Ge$_3$. Indeed, according to the 18-$n$ rule$^{16}$, each Fe atom tends to form the closed 18-electron configuration through the regular $\sigma$-type Fe-Ge bonds. When there are exclusively Fe-Ge bonds, 18 valence electrons per Fe atom would be required to maintain the 18-electron configuration. At the same time, the formation of special Fe-Fe bonds, which have a multicenter nature involving Ge atoms, and which are isolobal to $\sigma$-type Fe-Fe bonds, reduces the required number of valence electrons to the value of 18-$n$, where $n$ is the number of such Fe-Fe bonds. 4 Fe-Fe contacts per Fe atom are observed in the crystal structure of Fe$_2$Ge$_3$, hence, 14 valence electrons are required in order to achieve the 18-electron configuration. Therefore, Fe$_2$Ge$_3$ obeys the 18-$n$ rule. The stability of this compound should be rooted in a pseudogap or even a real band gap in the vicinity of the Fermi energy as demonstrated below by electronic structure calculations.
Electronic structure

Crystal structure parameters were used to perform electronic structure calculations for Fe₂Ge₃ with the ideal chimney ladder structure of the Ru₂Sn₃-type. The calculated density of states, which is shown in the left panel of Figure 6, consists mainly of the Fe 3d and Ge 4s and 4p contributions. The 14 electron rule formulated for NCLs,¹⁸ prior the 18-n rule was invented, is based exactly on this set of valence orbitals. The calculations confirm that the interaction of the Fe 3d with Ge 4s and 4p orbitals is responsible for the chemical bonding and leads to the formation of a narrow band gap. Analysis of partial contributions shows that the Fe 3d and Ge 4p states form the edges of the band gap (inset of Figure 6). The Ge 4s orbitals contribute significantly in the energy region between -13 eV and -7 eV only, forming the pocket of bonding states.

Band dispersion curves calculated for Fe₂Ge₃ are shown in the right panel of Figure 6. Here, a narrow band gap of 0.11 eV separating the valence and conduction bands is observed. The top of the valence band is formed by an almost parabolic maximum of the Ge 4p band located at the $\Gamma$ point of the Brillouin zone. At the same time, the bottom of the conduction band consists mainly of the flat Fe 3d states with the minimum also located at the $\Gamma$ point. It should be noted here that our results differ significantly from the data obtained by Sato et al.²² who carried out optimization of the Fe₂Ge₃ structural parameters assuming the Ru₂Sn₃-type of crystal structure and performed calculations using the FP-LAPW PBE GGA approach. The latter calculations predict the value of a band gap of 0.2 eV, which is twice higher than the value calculated in our study using the experimental structure parameters obtained at 100 K. We also found different location of bands on the band dispersion curves plot.

Spin-polarized electronic structure calculations with the ferromagnetic and antiferromagnetic initial spin configurations converge to the non-magnetic state evidencing against the formation of local moments in Fe₂Ge₃ and confirming that the non-magnetic configuration is lowest in energy. In summary, our electronic structure calculations show that Fe₂Ge₃ is a non-magnetic direct band semiconductor, in which the excitation of electrons from the steep Ge 4p bands to the more atomic-like flat Fe
3$d$ bands is observed. This flat character of the compact Fe 3$d$ bands underlies the formation of sharp peaks of the density of states on the band edges and, therefore, high values of the Seebeck coefficient for Fe$_2$Ge$_3$. Thermoelectric performance of Fe$_2$Ge$_3$ was analyzed within the Boltzmann transport theory by Sato et al. who found the theoretical values of $S$ as low as -250 $\mu$V/K at 500 K for the case of $n$-type doping.\textsuperscript{22} In order to resolve the behavior of Fe$_2$Ge$_3$, its transport properties have been studied in this work. Unfortunately, we did not succeed in the preparation of single crystals that are large enough for the measurements, thus only polycrystalline samples were investigated. Transport properties were measured on polycrystalline samples of FeGe$_\gamma$ ($\gamma = 1.5$) that possess the incommensurately modulated structure in contrast to single crystalline Fe$_2$Ge$_3$ with the ideal chimney ladder structure.

**Transport and magnetic properties**

Temperature-dependent resistivity, Seebeck coefficient, and thermal conductivity are shown in Figure 7. Resistivity of FeGe$_\gamma$ decreases with increasing temperature, and the slope of the $\rho(T)$ curve changes significantly with temperature. Accordingly, three different temperature regimes can be found on the $\rho(T)$ curve (Figure 7a). The first is characterized by the fast drop of the resistivity when the temperature is increased from 2 K to $\sim$ 100 K. In the second regime, between 100 K and 370 K, the resistivity is almost temperature-independent. Finally, in the third regime above 370 K, resistivity decreases again with increasing temperature following activation behavior. To interpret these complex features, we compare the $\rho(T)$ data measured for FeGe$_\gamma$ with the temperature-dependent resistivity of FeGa$_3$.\textsuperscript{42} In the case of FeGa$_3$, which is a semiconducting intermetallic compound with a narrow band gap of 0.5 eV, the $\rho(T)$ curve is not following simple activation behavior too. Rather, the resistivity of FeGa$_3$ is influenced by the presence of impurity bands\textsuperscript{43} that render the slope of the $\rho(T)$ curve. Analogous to FeGa$_3$, we assume the presence of impurity states located within the band gap of FeGe$_\gamma$ that promote electronic transport. Then, the first low-temperature regime reflects activation of charge carriers from the valence band to the impurity bands. The second, mid-temperature regime reflects saturation of the impurity bands, and the temperature-independent resistivity
is observed. Finally, when the impurity bands are filled, the activation of charge carriers to the conduction band is observed. The inset of Figure 7a shows the resistivity as the $\ln \rho(1/T)$ plot. On this plot, the linear behavior is observed at high temperatures yielding $E_g = 0.03$ eV. This value is in qualitative agreement with the results of electronic structure calculations, which predict the gap of 0.11 eV for Fe$_2$Ge$_3$ with an ideal chimney ladder structure. The discrepancy may be caused by the well-known overestimate of the band gap in LDA calculations and by additional peculiarities of polycrystalline FeGe$_\gamma$ with its incommensurately modulated structure. Nevertheless, the observed linear slope on the $\ln \rho(1/T)$ plot indicates that the semiconducting behavior is an inherent feature of both commensurate Fe$_2$Ge$_3$ and polycrystalline FeGe$_\gamma$. Such a behavior appears at high temperatures when impurity bands saturate.

The semiconducting behavior seen in the resistivity data is corroborated by the measurements of the Seebeck coefficient (Figure 7b). The Seebeck coefficient of FeGe$_\gamma$ is negative in the examined temperature range, while its absolute value gradually increases with increasing temperature reaching $|S| = 190 \mu$V/K at $T = 400$ K. This value is not in agreement with the $S(T)$ data presented in Ref. [22] probably due to the difference in sample preparation routes. The measured $S(T)$ dependence is monotonic below $T = 400$ K, however, a broad minimum of $S$ values is observed at higher temperatures $T \approx 600-620$ K. According to the empirical rule, the $S(T)$ dependence of a semiconductor should exhibit an extremum, at which the temperature is roughly corresponds to 1000 $E_g$, where the temperature is in K units, and $E_g$ is in eV. According to this "1000 $E_g$" formula, the value of $E_g \sim 0.6$ eV is supposed for FeGe$_\gamma$, which is not in agreement with the results of electronic structure calculations. In our opinion, the misfit comes from the large uncertainty of the "1000 $E_g$" formula.

When compared to simple metallic conductors that typically show absolute values of the Seebeck coefficient in the range of 5-20 $\mu$V/K, the values of $|S|$ for FeGe$_\gamma$ are significantly higher. Other T-E intermetallics, which are narrow-gap semiconductors, also exhibit high values of $|S|$ at elevated temperatures. For instance,
the values of $|S| = 400 \, \mu V/K$, 180 $\mu V/K$, and 420 $\mu V/K$ at 400 K were observed for FeGa$_3$, RuGa$_3$, and OsGa$_3$, respectively. As a consequence, such intermetallic compounds can be used in high-temperature thermoelectric materials. For instance, solid solutions based on RuIn$_3$ exhibit high values of $|S|$, and the dimensionless figure-of-merit $ZT = 0.8$ was achieved at high temperatures for RuIn$_{3-y}$Zn$_y$ with $y = 0.025$. The potential use of FeGe$_{\gamma}$ as a high-temperature thermoelectric material was considered by Sato et al., who found by semi-empirical calculations that $ZT$ values above 1.0 can be achieved in this material when the electron count is optimized.

Another important feature of the polycrystalline FeGe$_{\gamma}$ that provides an additional path to high thermoelectric performance is the low glass-like thermal conductivity observed in the broad temperature range. In our study, the observed $\kappa$ is not exceeding 1 W m$^{-1}$ K$^{-1}$ in the temperature range of 4-400 K (Figure 7b). Such a low thermal conductivity can be compared to that of skutterudites and thermoelectric clathrates. The concept of a phonon crystal, where heavy rattling atoms are placed in spacious cages leading to an effective phonon relaxation, explains the low thermal conductivity of such materials as, for instance, in the Yb$_x$Co$_{2.5}$Fe$_{1.5}$Sb$_{12}$ skutterudite and R$_8$Ga$_{16}$Ge$_{30}$ (R = Sr, Eu) clathrates. Here, we can assume that complex features of the crystal structure, including its incommensurability, may also cause low thermal conductivity that was independently observed for FeGe$_{\gamma}$ in this study, and in the literature.

Magnetic susceptibility $\chi(T)$ of Fe$_2$Ge$_3$ single crystals measured in the temperature range between 2 K and 300 K in 7 T magnetic field is presented in Figure 8. The susceptibility is temperature-independent within its error bar at temperatures above 50 K. Below ~50 K a small upturn of $\chi(T)$ is observed, which probably is due to the presence of tiny amounts of paramagnetic impurities. For the temperature dependence of magnetic susceptibility of Fe$_2$Ge$_3$, different scenarios can be proposed compared to other narrow-gap intermetallic semiconductors. For instance, FeSb$_2$ exhibits nearly temperature-independent magnetic susceptibility at low temperatures and thermally activated $\chi(T)$ at higher temperatures. For FeSi, a combination of the Curie-Weiss paramagnetic and activated behavior is observed in a
wide temperature range.\textsuperscript{4} Finally, CrSb\textsubscript{2} exhibits $\chi(T)$, which is very similar to that of FeSb\textsubscript{2},\textsuperscript{48} but in contrast to its Fe-based analog, CrSb\textsubscript{2} orders antiferromagnetically below $T_N = 273$ K.\textsuperscript{49} In the case of Fe\textsubscript{2}Ge\textsubscript{3}, the observed $\chi(T)$ is temperature-independent at $T > 50$ K and very low in magnitude, which is consistent with the scenario of a non-metallic system with relatively small concentration of charge carriers and without the preformed local magnetic moments. Thus, the experimental magnetic susceptibility of single crystals of Fe\textsubscript{2}Ge\textsubscript{3} corroborates its narrow-gap semiconducting behavior deduced from the measurements of resistivity and by the electronic structure calculations.

\textbf{Conclusions}

Chemical transport approach was utilized to synthesize the Nowotny chimney ladder compound Fe\textsubscript{2}Ge\textsubscript{3}. With iodine as transport agent, polycrystalline samples of FeGe$_\gamma$ can be prepared on a par with other synthetic techniques. According to the TEM studies, the obtained samples of FeGe$_\gamma$ ($\gamma = 1.5$) possess both the commensurate and incommensurately modulated chimney ladder structures, significantly hindering the interpretation of the X-ray powder patterns. Combined use of I$_2$ and Mo(CO)$_6$ transport agents in the temperature gradient affords single crystals of the target compound to be grown for the first time, so that its crystal structure could be finally resolved. Remarkably, stoichiometric Fe\textsubscript{2}Ge\textsubscript{3} features a commensurate chimney ladder structure of the Ru\textsubscript{2}Sn\textsubscript{3}-type. Using single-crystal data, we demonstrated that Fe\textsubscript{2}Ge\textsubscript{3} obeys the 18-\textit{n} rule formulated for the T-E intermetallic compounds, and electronic structure calculations qualify Fe\textsubscript{2}Ge\textsubscript{3} as a narrow-gap semiconductor in compliance with the 18-\textit{n} rule. Temperature-dependent resistivity and Seebeck coefficient measurements corroborate the semiconducting behavior. From activated behavior of the resistivity a band gap of 30 meV is estimated, and high absolute values of the Seebeck coefficient are observed at elevated temperatures. Along with substantially low thermal conductivity below 1 W m\textsuperscript{-1} K\textsuperscript{-1}, these observations place Fe\textsubscript{2}Ge\textsubscript{3} in a class of prospective thermoelectric materials. The new synthetic route developed in our study should foster further optimization of thermoelectric performance in future studies of this interesting material.
Acknowledgements

The authors thank Dr. Sergey Kazakov and Oleg Tyablikov for their help with the PXRD experiments. V.Yu.V. appreciates the help of Dr. Sergey Dorofeev in provision and handling of the Mo(CO)$_6$ reagent. The work is supported by the Russian Science Foundation, grant No. 17-13-01033. V.Yu.V. appreciates the support from the European Regional Development Fund, project TK134. A.A.T. acknowledges financial support by the Federal Ministry for Education and Research under the Sofja Kovalevskaya Award of the Alexander von Humboldt Foundation. E.V.D. thanks the National Science Foundation, grant No. CHE-1152441.


[35] Rohrer, F.E.; Lind, H.; Eriksson, L.; Larsson, A.-K.; Lidin, S. Incommensurately Modulated Nowotny Chimney-Ladder Phases: Cr1,3Mo0.75Ge1.75 with χ = 0.65 and 0.84. Z. Kristallogr. 2001, 216, 190-198.

Table 1. Crystal data collection and refinement details for Fe$_2$Ge$_3$ at 100 K.

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<td>formula weight (g mol$^{-1}$)</td>
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Table 2. Atomic coordinates and thermal displacement parameters for the crystal structure of Fe$_2$Ge$_3$ at 100 K.

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<th>atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$ (Å$^2$)</th>
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<td>Fe1</td>
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<td>0.0022(2)</td>
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<td>0.08497(12)</td>
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<td>0.17682(13)</td>
<td>1/4</td>
<td>0.00242(18)</td>
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Table 3. Selected interatomic distances in the structure of Fe$_2$Ge$_3$ at 100 K.

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<th>Bond</th>
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<td>Fe2 –Ge1 (4×)</td>
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<td>Ge2 –Ge1 (2×)</td>
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<td>–Ge2 (1×)</td>
<td>2.793(2)</td>
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**Fig. 1.** Part of the Fe-Ge phase diagram with Ge concentrations of > 30 at.%.

**Fig. 2.** PXRD patterns of FeGe$_\gamma$ alloys near the stoichiometric composition of $\gamma = 1.5$. Peak positions of FeGe ($P2_13$, FeSi-type) and Ge phases are marked with hash marks and asterisks, respectively. Black line at the bottom display the theoretical PXRD pattern of Fe$_2$Ge$_3$ with the commensurate Ru$_2$Sn$_3$-type crystal structure (for more details, see the section **Crystal structure: single crystals**).

**Fig. 3.** SAED patterns taken along [010], [100], and [001] directions for the commensurate orthorhombic phase.
Fig. 4. (a)-(c) Representative SAED patterns of FeGe\(_\gamma\) along the [1-10], [100] and [001] directions for the incommensurately modulated phase. The insets show enlargements of the parts indicated on the figures, except the inset indicated by a black border, which is an enlargement of an SAED pattern from another crystal for comparison. (d) HAADF-STEM image of a typical FeGe\(_\gamma\) crystal. The white lines indicate the shift of the Ge helices in successive Fe chimneys. (e) Enlarged view of (d), including an image calculated using the model found for the Fe\(_2\)Ge\(_3\) single crystal structure (for more details, see the section **Crystal structure: single crystals**). Slight differences are visible due to the incommensurate character of FeGe\(_\gamma\).
Fig. 5. (a) View of the Fe$_2$Ge$_3$ crystal structure along the [001] (left) and [100] (right) directions. (b) Coordination polyhedra of Fe atoms.

Fig. 6. (Left) Density of states plot calculated for Fe$_2$Ge$_3$. The contributions of Fe and Ge species are represented by the red and blue lines, respectively. The inset shows the region near the Fermi energy. On the inset, the contributions of the Fe 3$d$ and Ge 4$p$ states are shown in orange and green colors, respectively. (Right) Electronic structure of Fe$_2$Ge$_3$ as obtained with the PW LDA. Partial contribution of the Fe 3$d$ states is shown in red color, and that of Ge 4$p$ states – in green color.
**Fig. 7.** (a) Temperature-dependent resistivity of FeGe$_{\gamma}$ ($\gamma = 1.5$). The inset shows resistivity as the $\ln \rho(1/T)$ plot, the red line represents a linear fit to the data. (b) Seebeck coefficient and thermal conductivity of FeGe$_{\gamma}$ ($\gamma = 1.5$).

**Fig. 8.** Magnetic susceptibility of Fe$_2$Ge$_3$ single crystals measured in 7 T magnetic field.
TOC graphic