Chiral Properties of Structure and Magnetism in $Mn_{1-x}Fe_xGe$ Compounds: When the Left and the Right are Fighting, Who Wins?

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Magnetic susceptibility measurements have shown that the compounds $Mn_{1-x}Fe_xGe$ are magnetically ordered through the whole range of concentrations $x = [0.0, 1.0]$. Small-angle neutron scattering reveals the helical nature of the spin structure with a wave vector, which changes from its maximum ($|\mathbf{k}| = 2.3\ \mathrm{nm}^{-1}$) for pure MnGe, through its minimum ($|\mathbf{k}| \to 0$) at $x_c \approx 0.75$, to the value of $|\mathbf{k}| = 0.09\ \mathrm{nm}^{-1}$ for pure FeGe. The macroscopic magnetic measurements confirm the ferromagnetic nature of the compound with $x = x_c$. The observed transformation of the helix structure to the ferromagnet at $x = x_c$ is explained by different signs of chirality for the compounds with $x > x_c$ and $x < x_c$. We used x-ray diffraction and polarized neutron scattering to evaluate the crystallographic chirality Γ_c and the magnetic chirality γ_m of the FeGe single crystals. Similar to previous observations for FeSi-based compounds, FeGe demonstrates left- (right-)handed crystalline chirality acompained by right (left) handedness of the magnetic helix ($\Gamma_c \gamma_m = -1$). At variance, MnSi related compounds show the opposite behavior ($\Gamma_c \gamma_m = 1$). Since the magnetic chirality γ_m relates to the sign of the Dzyaloshinskii-Moriya interaction (DMI), for the same geometrical arrangement (Γ_c) the sign of DMI can be set by the proper choice of the transition metal.

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The crystalline and magnetic structures of MnSi and doped monosilicides of Mn and Fe ($Mn_{1-x}Fe_xSi$, $Mn_{1-x}Co_xSi$, and $Fe_{1-x}Co_xSi$) are very well established nowadays. All these compounds have the same B20 type cubic noncentrosymmetric crystallographic structure described by the chiral $P2_13$ space group. The chiral Dzyaloshinskii-Moriya (DM) interaction stabilizes the spiral spin structure in these systems below T_c [1,2]. Systematic studies [3–7] have shown that the sense of the structural chirality (left or right) rigorously determines the sense of the magnetic chirality via the sign of the DM interaction. However, the relation between two chiralities is found to be different for various B20 compounds. For Mn-based compounds ($Mn_{1-x}Fe_xSi$ and $Mn_{1-x}Co_xSi$) the crystalline and magnetic chiralities have the same sense, while for the Fe-based ones ($Fe_{1-x}Co_xSi$) the chiralities are opposite to each other [3–7]. One can conclude that the two types of compounds, Mn and Fe based, posses different signs of the DM interaction for the crystals of the same chirality. An intriguing experiment for proof of this hypothesis would be the change of the chirality sense in the $Mn_{1-x}Fe_xSi$ family by changing the Mn to Fe ratio. Unfortunately, the pure FeSi is not magnetically ordered, so the $Mn_{1-x}Fe_xSi$ family shows the spin ordering only in a narrow range of $x \in [0, 0.17]$, and further Fe doping leads to magnetic disorder.

A good candidate to follow the change of the magnetic chirality is the $Mn_{1-x}Fe_xGe$ family with B20 structure. The pure compounds (FeGe [8] and MnGe [9–11]) and, as we show in this Letter, all $Mn_{1-x}Fe_xGe$ monogermanides are magnetically ordered. Here, we report on the experimental evidence for magnetic transition in the $Mn_{1-x}Fe_xGe$ compounds, where the helix chirality can be altered by mixing the two types of magnetic atoms (Fe and Mn).

We used x-ray diffraction [12,13] and polarized neutron scattering [14,15] to evaluate the crystallographic chirality Γ_c and the magnetic chirality γ_m of the FeGe single crystal. A single crystal with the size of $1 \times 1 \times 1\ \mathrm{mm}^3$ was measured with neutrons and, afterwards, it was polished to 50 μm and investigated using x-ray diffraction. The experiment was done using synchrotron radiation with ($\lambda = 0.7$ Å) at the Swiss-Norwegian Beam Line BM1A of the ESRF (Grenoble, France) with the PILATUS@SNBL diffractometer. The protocol similar to that used in Refs. [5–7] has been applied for the data analysis.

The FeGe sample was identified as having $P2_13$ symmetry with the structural parameters $u_{\mathrm{Fe}} = 0.1358(3)$

and $u_{Ge} = 0.8415(2)$ and the lattice constant $a = 0.469801(18)$ nm. Low R factors together with a well-defined Flack parameter [0.07(9)] confirm that the absolute structure has been determined correctly [16]. According to the definition given in Ref. [17], the crystal is left-handed with $u_{Fe} = 0.1358(3)$ [LHC, the left-handedness Γ_c is denoted as $(-)$].

Using polarized neutron diffraction one can determine the spin chirality of a magnetic system [14,15]. To quantify the helix chirality γ_m we define the polarization of the scattered neutrons P_s at a fixed point in the momentum space $\mathbf{Q} = \mathbf{k}$ as the following [5]:

$$P_s(\mathbf{k}) = \frac{I^+(\mathbf{k}) - I^-(\mathbf{k})}{I^+(\mathbf{k}) + I^-(\mathbf{k})} = \gamma_m P_0, \qquad (1)$$

where I^+ and I^- are the intensities of the scattered beam with initial polarization $\mathbf{P}_0$ parallel and antiparallel to the scattering vector $\mathbf{Q}$, respectively. The sign of γ_m reflects the sense of chirality (left-or right-handed). The value of γ_m is proportional to the difference between left- and right-handed domains. $|\gamma_m| = 1$ corresponds to a single domain enantiomorph, $|\gamma_m| = 0$ corresponds to equally distributed left- and right-handed domains in a racemate sample.

The polarized small-angle polarized neutron scattering (SANS) was performed using the D22 instrument at the ILL (France). A polarized neutron beam with initial polarization $P_0 = 0.93$ and mean wavelength $\lambda = 0.60$ nm was used. A weak magnetic field (1 mT) guiding the polarization $\mathbf{P}_0$ was applied along $\mathbf{Q}_x$. Figure 1 shows a typical SANS map from the MnSi sample at the temperature below T_c with initial polarization opposite to $-\mathbf{P}_0$ [Fig. 1(a)] and along $+\mathbf{P}_0$ [Fig. 1(b)] the magnetic field. This MnSi crystal is known to show a left-handed crystallographic configuration and also a left-handed spin helix [5]. The MnSi sample and its scattering maps are considered as a standard of measurements. For this sample γ_m was obtained to be equal to 1 ± 0.01 in the whole temperature range $T < T_c$. The similar SANS maps for the FeGe sample are shown in Figs. 1(c) and 1(d) at T below T_c. Comparing Figs. 1(a) and 1(b) with Figs. 1(c) and 1(d) one can conclude that this FeGe sample has the opposite sense of chirality to this MnSi sample; i.e., it has right-handed helix. This spin helix is opposite to the crystalline chirality Γ_c determined for this FeGe sample by x rays. So, we have established that the magnetic chirality of the FeGe crystal is opposite to the crystallographic counterpart ($\Gamma_c \gamma_m = -1$). This behavior is in accordance with the Fe-based monosilicides $Fe_{1-x}Co_xSi$, [5] and it is opposite to the Mn-based monosilicides [6].

As already mentioned, we have synthesized the $Mn_{1-x}Fe_xGe$ compounds (with x running from 0.0 to 1.0). As they can only be synthesized under high pressure, samples are in a polycrystalline powder form with a crystallite size not less than a micron (see Ref. [18] for details). The x-ray powder diffraction confirmed the B20 structure of these samples and showed traces of impurities less than 1%–2% in volume fraction. The magnetic properties of the samples were measured by SQUID magnetometry and small-angle neutron scattering. Figure 2 shows the temperature dependence of the susceptibility χ taken at $H = 50$ mT for the compounds with $x = 0, 0.25, 0.5, 0.75, 1.0$.

As it was shown for the MnSi-based compounds with helical structure, the temperature driven transition from the paramagnetic to the helical phase goes through a chiral fluctuating state associated with a maximum of the susceptibility χ (see Ref. [19] for more explanations). Four susceptibility curves in Fig. 2 have the shape with a maximum, which is typical for a helical magnets. We determined the critical temperatures T_c from these dependences

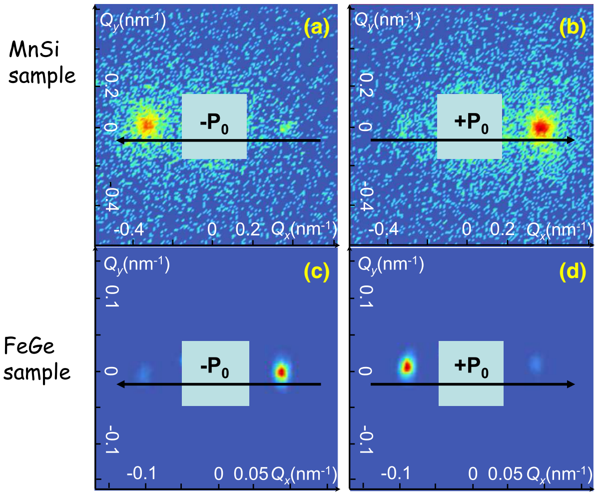

FIG. 1 (color online). Maps of the SANS intensities of a MnSi sample (standard crystal) at $T = 25$ K and the FeGe crystal under study at $T = 260$ K for the polarization $\mathbf{P}_0$ opposite to the guide field (a), (c) and along it (b), (d).

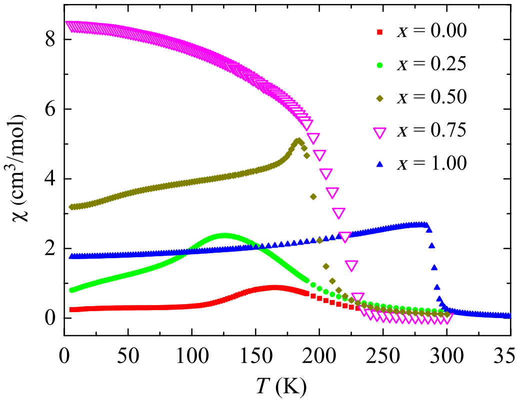

FIG. 2 (color online). Temperature dependence of the susceptibility χ at an applied magnetic field of 50 mT for the compounds with $x = 0, 0.25, 0.5, 0.75, 1.0$. For better visibility the susceptibility of the compounds with $x = 0$ and $x = 0.25$ are multiplied by a factor of 10 and that of the compound with $x = 0.5$ is multiplied by a factor of 5.

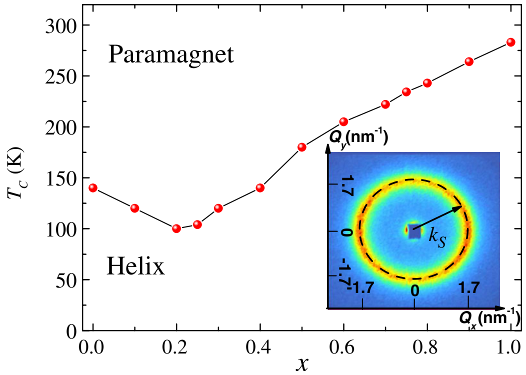

FIG. 3 (color online). Dependence of the critical temperature T_C on the concentration x of $\mathrm{Mn}_{1\text{-}x}\mathrm{Fe}_x\mathrm{Ge}$ compounds. Inset: Example of a SANS map for the compound with $x = 0.3$.

as the low-temperature inflection point in the T dependence, which corresponds to the maximum of the first derivative of the susceptibility on temperature $d\chi/dT$. One curve corresponding to $x_{\mathrm{Fe}} = 0.75$ (highlighted by bigger, down-pointing triangular symbols) has a Curie-Weiss shape, which is typical for ferromagnets, without any maximum. The critical temperature (Curie temperature) determined from this curve is $T_C = 234.3$ K. The critical temperatures T_c versus the concentration x are presented in Fig. 3. T_c decreases slightly on increase of x up to 0.3, then it monotonically increases to 278 K.

The T_c values determined from the susceptibility curves are confirmed by SANS measurements. The scattering maps exhibit a ring corresponding to the scattering from randomly oriented spiral domains with the same helix wave vector $\mathbf{k}$. The inset in Fig. 3 shows an example of a SANS map for one compound. The helix wave vectors for all the compounds were obtained from the SANS maps by circular averaging.

The momentum transfer dependences of the scattering intensity $I(Q)$ are shown for different compounds in Fig. 4.

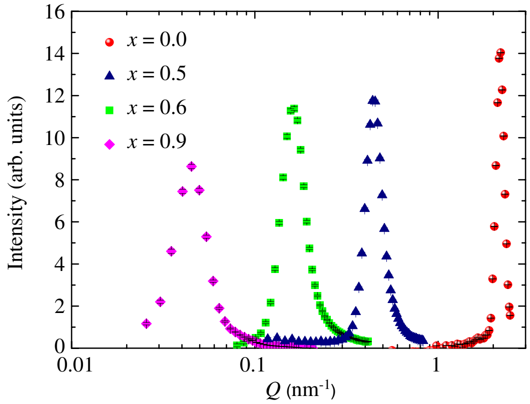

FIG. 4 (color online). Momentum transfer dependence of the SANS intensity at $T \approx 20$ K for compounds with $x = 0$, 0.5, 0.6, 0.9.

In order to better visualize the dramatic change of the diffraction peak position k_s of 2 orders of magnitude, we plotted the argument Q in a logarithmic scale. Figure 5 shows an unusual x dependence of the helix wave vector. In the Mn-rich compounds k_s does not change much for $x \in [0, 0.4]$, then it falls down to $k_s = 0$ at $x \approx 0.75$, and increases again up to the value of $k = 0.09\ \mathrm{nm}^{-1}$ for pure FeGe.

As is well known, the wave vector of the helix $k_s = SD/J$ is a measure of the ratio between the isotropic spin exchange interaction described by the effective exchange constant J ($J > 0$ for ferromagnets) and the DM interaction with the constant D [2]. S is the average spin per unit cell. The sign of the wave vector $\mathbf{k}$ describes the chirality of the helical structure and is directly determined by the sign of the Dzyaloshinskii constant $\mathrm{sgn}(D)$.

Accounting for the fact that the value of k approaches zero at $x_c \approx 0.75$ and the ordering temperature is as high as $T_c = 234.3$ K, we conclude that this compound is a ferromagnet in accordance with the magnetic measurements shown in Fig. 2. This can only be possible when the macroscopic Dzyaloshinskii constant D is effectively vanishing. Because for this noncentrosymmetric system the DM interaction is not zero at the atomic scale, we could suggest that two types of DM interactions of positive and negative signs compete and compensate each other effectively on the scale of the helix pitch $d = 2\pi/k_s$.

In any case, the x dependence of the wave vector k_s in the Fe-rich part of compounds (Fig. 5) can now be interpreted as a change of the sign of $\mathbf{k}$ at $x \approx 0.75$. Such a change of sign indicates that the sign of the DM interaction is altered in the present series of compounds. Since we have found for FeGe that the left-handed crystal is connected to the right-handed spin helices, the opposite must hold for concentrations smaller than $x_c \approx 0.75$. Therefore, for MnGe the left-handed crystals should correspond to the left-handed spin helices.

These findings concerning $\mathrm{Mn}_{1\text{-}x}\mathrm{Fe}_x\mathrm{Ge}$ compounds are summarized in Table I with similar conclusions as for the monosilicides of the transition metals (MnSi- and

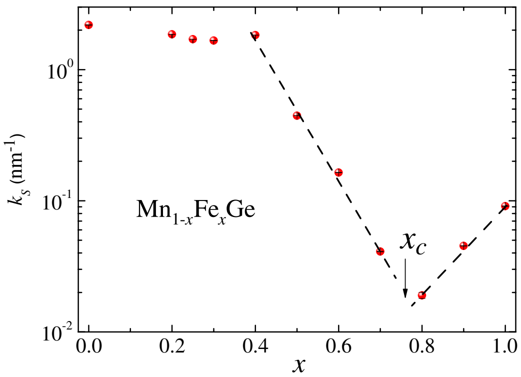

FIG. 5 (color online). Dependence of the helix wave vector k_s on the concentration x.

TABLE I. Crystal chirality Γ_c and magnetic chirality γ_m of the compounds with the $P2_13$ structures. (+1) and (−1) correspond to the right and left chirality, respectively.

Compound	$\Gamma_c \rightarrow \gamma_m$	$\Gamma_c \gamma_m$
MnSi	$1(-1) \rightarrow 1(-1)$	1 [5]
FeSi	$1(-1) \rightarrow -1(1)$	−1 [6,7]
FeGe	$1(-1) \rightarrow -1(1)$	−1 (this Letter)
MnGe	$1(-1) \rightarrow 1(-1)$	1 (this Letter)

FeSi-based compounds). We note that the FeGe crystal has opposite signs of crystal and magnetic chiralities similar to the FeSi-based compounds. Referring to the change of sign of the DM interaction in the $Mn_{1-x}Fe_xGe$ compounds, MnGe crystals have the same signs for crystalline and magnetic chirality in accordance with the MnSi-based compounds. Consequently, the sign of the DM interaction depends on the $3d$ element occupying the metal site.

The interaction of structural and magnetic chiralities is also expected for more complex than spiral magnetic structures like Skyrmions and have potential relevance for related magnetic phenomena such as a spin transfer torque [20]. We have to admit that we are not aware of any microscopic mechanism that could mediate this interaction and tie the value of $\Gamma\gamma$ to the identity of the $3d$ metals (Mn or Fe). It may be related to the recent theoretical conjecture on the local character of magnetization [21]; *ab initio* calculations of DM interactions are definitely needed to shed light on the microscopic origin for coupling structural and magnetic chirality [22]. It is probable that a symmetry analysis of the DM interaction in B20-type crystals can reveal a nontrivial character of tilting the Mn(Fe) moments [23]. It is also suggested that the competition between exchange interactions for neighboring and next-neighboring magnetic atoms could reverse the effective D constant even if DM interaction does not change at the interatomic scale [24]. An evidence for the concentration dependence of the exchange interactions is the drastic concentration dependence of T_c (Fig. 3).

Answering the question in the title—when the left and the right are fighting, who wins?—we conclude that the compound with $x_c \approx 0.75$ becomes *ferromagneticlike* in a sense that $k_s \rightarrow 0$ in the spin spiral structure. The magnetic properties of the compounds with x close to x_c may not be trivial. The fact that the critical concentration x_c is roughly 0.75 and not 0.5 (the composition with a maximal degree of disorder) is not surprising because of very strong difference (25 times) between k_s for pure MnGe and FeGe as well as the difference between the values of the ordered magnetic moment per atom, which are $2.3\mu_B$ in MnGe and $1.0\mu_B$ FeGe compounds [11,25]. In the simple model the DM interaction depends on the vector product of neighboring atomic moments, while DM constant (D) is determined by the geometrical configuration of the local atomic structure [26]. Further theoretical and experimental studies should discover the complexity of phenomena related to and determined by the mixture of chiralities in these compounds.

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[1] I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. **46**, 1420 (1964).
[2] P. Bak and M. H. Jensen, J. Phys. C **13**, L881 (1980).
[3] M. Tanaka, H. Takayoshi, M. Ishida, and Ya. Endoh, J. Phys. Soc. Jpn. **54**, 2970 (1985).
[4] M. Ishida, Ya. Endoh, S. Mitsuda, Yo. Ishikawa, and M. Tanaka, J. Phys. Soc. Jpn. **54**, 2975 (1985).
[5] S. V. Grigoriev, D. Chernyshov, V. A. Dyadkin, V. Dmitriev, S. V. Maleyev, E. V. Moskvin, D. Menzel, J. Schoenes, and H. Eckerlebe, Phys. Rev. Lett. **102**, 037204 (2009).
[6] S. V. Grigoriev, D. Chernyshov, V. A. Dyadkin, V. Dmitriev, E. V. Moskvin, D. Lamago, Th. Wolf, D. Menzel, J. Schoenes, S. V. Maleyev, and H. Eckerlebe, Phys. Rev. B **81**, 012408 (2010).
[7] V. A. Dyadkin, S. V. Grigoriev, D. Menzel, D. Chernyshov, V. Dmitriev, J. Schoenes, S. V. Maleyev, E. V. Moskvin, and H. Eckerlebe, Phys. Rev. B **84**, 014435 (2011).
[8] B. Lebech, J. Bernhard, and T. Freltoft, J. Phys. Condens. Matter **1**, 6105 (1989).
[9] N. Kanazawa, Y. Onose, T. Arima, D. Okuyama, K. Ohoyama, S. Wakimoto, K. Kakurai, S. Ishiwata, and Y. Tokura, Phys. Rev. Lett. **106**, 156603 (2011).
[10] N. Kanazawa, J.-H. Kim, D. S. Inosov, J. S. White, N. Egetenmeyer, J. L. Gavilano, S. Ishiwata, Y. Onose, T. Arima, B. Keimer, and Y. Tokura, Phys. Rev. B **86**, 134425 (2012).
[11] O. L. Makarova, A. V. Tsvyashchenko, G. Andre, F. Porcher, L. N. Fomicheva, N. Rey, and I. Mirebeau, Phys. Rev. B **85**, 205205 (2012).
[12] H. D. Flack, Acta Crystallogr. Sect. A **39**, 876 (1983).
[13] H. D. Flack, Acta Crystallogr. Sect. A **55**, 908 (1999).
[14] S. V. Maleyev, V. G. Bar'yahtar, and R. A. Suris, Sov. Phys. Solid State **4**, 2533 (1962).
[15] M. Blume, Phys. Rev. **130**, 1670 (1963).
[16] We note that the Flack parameter is a measure of the inversion twinning. For Flack parameter equal to zero, the absolute structure is determined correctly; for Flack parameter equal to one, the absolute structure has to be inverted. For Flack parameter between zero and one, the crystal is a mixture of domains of both opposite chirality.
[17] V. Dmitriev, D. Chernyshov, S. Grigoriev, and V. Dyadkin, J. Phys. Condens. Matter **24**, 366005 (2012).
[18] A. V. Tsvyashchenko, J. Less-Common Met. **99**, L9 (1984).

[19] S. V. Grigoriev, E. V. Moskvin, V. A. Dyadkin, D. Lamago, T. Wolf, H. Eckerlebe, and S. V. Maleyev, Phys. Rev. B **83**, 224411 (2011).

[20] F. Jonietz *et al.*, Science **330**, 1648 (2010).

[21] S. V. Demishev *et al.*, Phys. Rev. B **85**, 045131 (2012).

[22] R. Takeda, S. Yamanaka, M. Shoji, and K. Yamaguchi, Int. J. Quantum Chem. **107**, 1328 (2007).

[23] V. E. Dmitrienko and V. A. Chizhikov, Phys. Rev. Lett. **108**, 187203 (2012).

[24] V. A. Chizhikov and V. E. Dmitrienko (to be published).

[25] R. Wappling and L. Haggstrom, Phys. Lett. A **28**, 173 (1968).

[26] S. V. Grigoriev, V. A. Dyadkin, E. V. Moskvin, D. Lamago, Th. Wolf, H. Eckerlebe, and S. V. Maleyev, Phys. Rev. B **79**, 144417 (2009).