Interplay between crystalline chirality and magnetic structure in Mn$_{1-x}$Fe$_x$Si

S. V. Grigoriev,[1] D. Chernyshov,[2,3] V. A. Dyadkin,[1] V. Dmitriev,[2] E. V. Moskvin,[1] D. Lamago,[4] Th. Wolf,[5] D. Menzel,[6] J. Schoenes,[6] S. V. Maleyev,[1] and H. Eckerlebe[7]

[1]*Petersburg Nuclear Physics Institute, Gatchina, 188300 St. Petersburg, Russia*
[2]*Swiss-Norwegian Beamlines, European Synchrotron Radiation Facility, Grenoble 38000, France*
[3]*Geological Faculty, St. Petersburg State University, 194900 St. Petersburg, Russia*
[4]*Laboratoire Léon Brillouin, 91191 Saclay, France*
[5]*Institut für Festkörperphysik, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany*
[6]*Institut für Physik der Kondensierten Materie, Technische Universität Braunschweig, 38106 Braunschweig, Germany*
[7]*GKSS Forschungszentrum, 21502 Geesthacht, Germany*
(Received 22 November 2009; published 29 January 2010)

X-ray diffraction using synchrotron radiation and polarized neutron small-angle diffraction have been used to evaluate the absolute crystallographic structure and the spin helix chirality of Mn$_{1-x}$Fe$_x$Si. Contrary to previous observations we show that left- and right-handed crystals can be found for MnSi and its iron substituted analogs. The structural chirality rigorously determines the magnetic chirality of these compounds: left-(right-)handed crystalline chirality establishes left (right) handedness of the magnetic helix.

From the energetic point of view two enantiomers should exist with equal probability. The inorganic processes involving chiral products commonly yield a racemic mixture of both enantiomers. Therefore, it is especially surprising that the first systematic study of the cubic noncentrosymmetric magnet MnSi and the related system Fe$_{1-x}$Co$_x$Si,[1] both having $P2_13$ symmetry, had shown a complete chiral symmetry breaking. Namely, seven MnSi crystals grown from different seeds and several Fe$_{1-x}$Co$_x$Si crystals have the same crystallographic handedness determined to be left. Although the authors of Ref. [1] had conceded that the surprising result is, perhaps, caused by the small number of samples, the study has resulted in a general belief in a complete chiral symmetry breaking in MnSi.

Normally an enantiomeric excess occurring in the experiment is related to the experimental setup growing a crystal from a seed.[2] As was recently shown,[3] the cubic magnet Fe$_{1-x}$Co$_x$Si with Dzyaloshinskii-Moriya (DM) interaction can exist in both left-handed and right-handed configurations; all the inspected crystals were grown by the Czochralski method and it can be shown that their chirality should depend to a large extent on the chirality of a seed crystal. These findings are in clear contradiction to what has been found previously for MnSi.

The presence of a close relationship between crystalline and magnetic structures is also worth noting: a left-handed atomic configuration found in Fe$_{1-x}$Co$_x$Si corresponds to a right-handed magnetic helix and, vice versa, a right-handed atomic configuration to a left-handed helix.[3] On the contrary, the reported left-handed crystallographic chirality of the MnSi coexists with a left-handed magnetic structure.[1,3] However, it is not obvious whether this correspondence is a universal property of MnSi as well as its doped analogs in both the left- and right-handed species.

In this Brief Report we demonstrate that (i) left and right forms of the pure MnSi and iron-doped crystals can be grown by the Czochralski and Bridgeman methods and (ii) the magnetic chirality of all Mn$_{1-x}$Fe$_x$Si crystals follows its crystallographic counterpart; the opposite to the relationship

has been found for a seemingly similar Fe$_{1-x}$Co$_x$Si compound.[3] These conclusions have been drawn on the basis of data collected using x-ray and polarized neutron diffraction on the samples grown by both Czochralski and Bridgeman methods. Three high-purity MnSi single crystals and nine crystals of Mn$_{1-x}$Fe$_x$Si with $x=0.06$, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.16, and 0.29 have been investigated. All 12 crystals were inspected by x-ray diffraction and eight of these 12 crystals using a polarized neutron-scattering technique.

The absolute structure and its chiral configuration were determined by properly collected single-crystal diffraction data[4,5] and the magnetic helicity is characterized by polarized neutrons.[6] The x-ray diffraction experiment was performed using synchrotron radiation with $\lambda=0.77$ Å at the Swiss-Norwegian BeamLine BM1A of the ESRF (Grenoble, France) with the KUMA6 diffractometer. Crystals with an average size of about 50 μm were prepared from the same batches as used for the neutron-scattering measurements. The ability of the x-ray diffraction experiment to distinguish between structures with opposite chirality originates from the resonance scattering contribution in the structural amplitudes. This contribution defines the wavelength-dependent inversion-distinguishing power (IDP) that is proportional to $[|F(\mathbf{H})|^2-|F(-\mathbf{H})|^2]$.[5] Since the IDP is wavelength dependent, the wavelength of synchrotron radiation has been set to $\lambda=0.77$ Å in order to balance inversion-distinguishing power and absorption effect. In our data analysis the absolute structure was determined by refining the Flack parameter[4] together with the inspection of the inverted structure. The Flack parameter f can be expressed via half-difference of the intensities of the Friedel equivalents:[4,5]

$$I(\mathbf{H}) - I(-\mathbf{H}) = (1 - 2f)[|F(\mathbf{H})|^2 - |F(-\mathbf{H})|^2]. \qquad (1)$$

Here I and F denote the intensity and the structural factor for the Bragg reflection $\mathbf{H}$, respectively. The Flack parameter may, therefore, be considered a measure of the ratio between domains of different handedness. A zero value of the Flack
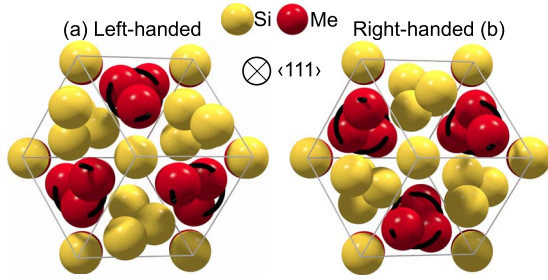
FIG. 1. (Color online) View of the crystal structure of MnSi [$P2_13$ structure with the atomic coordinates $(u,u,u),(1/2+u,1/2-u,-u),(1/2-u,-u,1/2+u),(-u,1/2+u,1/2-u)$] along the (111) axis for $u_{Me}=0.137$ and $u_{Si}=0.845$ (a) and for $u_{Me}=0.863$ and $u_{Si}=0.155$. (b) The chirality of the Si sublattice is left handed for the atomic configuration in (a) and right handed for the atomic configuration in (b).

parameter indicates an enantiopure sample with a correct absolute structure. For a Flack parameter equal to 1 the crystal structure has to be inverted.

Knowing the absolute structure one can easily determine the crystallographic handedness by means of the chiral configuration for the Mn and Si sublattices. Note that the crystallographic positions of Mn and Si in the $P2_13$ space group [Wyckoff position 4a (u,u,u)] are close to be related to an inversion symmetry ($u_{Si} \sim 1-u_{Mn}$). The two sublattices have, therefore, the opposite chirality. Figure 1 shows the view of the MnSi crystal [$P2_13$ structure with the atom coordinates $(u,u,u),(1/2+u,1/2-u,-u),(1/2-u,-u,1/2+u),(-u,1/2+u,1/2-u)$] along the (111) axis (a) for a sample with $u_{Mn}=0.135$ and $u_{Si}=0.845$ and (b) for a sample with $u_{Mn}=0.865$ and $u_{Si}=0.155$. The Mn atoms form a helix skewing around (111) axis in a right-handed configuration for $u_{Mn}=0.135$ [Fig. 1(a)] and in a left-handed configuration for $u_{Mn}=0.865$ [Fig. 1(b)]. Si atoms form a helix around

(111) but, as expected, of opposite handedness. In the following we denote the $P2_13$ structure with the parameters $u_{Mn}=0.135$ and $u_{Si}=0.845$ as crystallographically left handed and the structure with the parameters $u_{Mn}=0.865$ and $u_{Si}=0.155$ as crystallographically right handed referring to the left-/right-handed skew of the Si sublattice. Similar conclusions can be drawn from the consideration of any other chiral object built from Mn or Si atoms; see a dodecaherlad coordination as an example.[7]

Two samples of pure MnSi grown by the Czochralski method and one sample grown by the Bridgeman method were first examined for their absolute structures. Two of these samples (Bridgeman and Czochralski) are identified as having $P2_13$ symmetry with the structural parameters $u_{Mn}=0.1370(1)$ and $u_{Si}=0.8456(1)$ and the lattice constant $a=0.456\,55(8)$ nm. Another crystal grown by the Czochralski method was clearly the opposite enantiomer with $u_{Mn}=0.8630(3)$ and $u_{Si}=0.1546(3)$ and with $a=0.456\,42(8)$ nm. Low R factors together with a well-defined Flack parameter on the order of 0.00(7) confirm that the absolute structure has been determined correctly. Similar data treatment and analysis have been performed for all $Mn_{1-x}Fe_xSi$ crystals. The lattice constant a of $Mn_{1-x}Fe_xSi$ decreases linearly upon increase in x in agreement with Vegard's law from $a=0.4565$ nm for MnSi toward $a=0.449$ nm for FeSi. The combined data set for atomic position of metal atoms u_{Me} is shown in Table I. According to the definition given above, there are eight left-handed crystals (LHCs) with $u_{Me}=0.137$ [the handedness Γ_c is denoted as (−)] and four right-handed crystals (RHCs) with $u_{Me}=0.867$ [their handedness Γ_c is denoted as (+)]. It is important to note that all the samples inspected by x-ray diffraction were either left- or right-handed enantiopure single-domain crystals.

Most of LHCs and only one of four RHCs lay in the concentration range $0.0 \leq x \leq 0.11$. One may conclude that the left handedness prevails for the crystals with the low Fe

TABLE I. Absolute positions of the metal and Si atoms (u_{Me} and u_{Si}) in the $P2_13$ structure along with the crystal handedness Γ_c and magnetic chirality γ_m of $Mn_{1-x}Fe_xSi$. Here (Br) and (Ch) denote the Bridgeman and Czochralski grown crystals, respectively. (+1) and (−1) correspond to the right and left handedness/chirality, respectively.

Compound	Method	u_{Me}	u_{Si}	Γ_c	γ_m
$x=0$	(Br)	0.1370(1)	0.8456(1)	−1	−1
$x=0$	(Ch)	0.1370(1)	0.8456(1)	−1	−1
$x=0$	(Ch)	0.8631(1)	0.1546(1)	+1	+1
$x=0.06$	(Br)	0.1368(1)	0.8454(1)	−1	−1
$x=0.08$	(Br)	0.1368(1)	0.8457(1)	−1	−1
$x=0.09$	(Ch)	0.1368(1)	0.8457(1)	−1	−1
$x=0.10$	(Br)	0.8630(1)	0.1547(1)	+1	+1
$x=0.11$	(Ch)	0.1368(1)	0.8457(1)	−1	−1
$x=0.12$	(Br)	0.1368(1)	0.8457(1)	−1	
$x=0.13$	(Br)	0.8630(1)	0.1546(1)	+1	
$x=0.16$	(Br)	0.1370(1)	0.8454(1)	−1	
$x=0.29$	(Br)	0.8632(1)	0.1552(1)	+1	

concentration (small x) while the right handedness is predominant for the crystals with high degree of substitution. On the other hand, even pure MnSi can be synthesized as both left- and right-handed crystals. This certainly dethrones the belief of the existence of only left-handed MnSi crystals in nature. Yet, the hypothesis of a tendency toward left handedness in MnSi crystals cannot be completely ruled out by our results.

Using polarized neutron diffraction one can determine the spin chirality of a magnetic system.[6] It can be measured as the difference between the scattering intensities taken from the incident neutron beam with the polarization along ($+P_0$ $=\mathbf{P_0}\mathbf{h}$) and opposite ($-P_0=\mathbf{P_0}\mathbf{h}$) to the guiding magnetic field $\mathbf{h}$ at a fixed position in the momentum space $\mathbf{Q}=\mathbf{k}$. The difference between two intensities at the same $\mathbf{Q}$ normalized to their sum, P_s, is used to quantify the helix chirality γ_m of the system:[3]

$$P_s(\mathbf{k}) = \frac{I(+P_0, \mathbf{k}) - I(-P_0, \mathbf{k})}{I(+P_0, \mathbf{k}) + I(-P_0, \mathbf{k})} = \gamma_m P_0, \qquad (2)$$

provided that $\mathbf{P_0} \| \mathbf{k}$.

The polarized small-angle neutron-diffraction measurements were done using the SANS2 instrument at the Geesthacht Neutron Facility (GeNF). A polarized neutron beam with initial polarization $P_0 = 0.93$, mean wavelength λ $= 0.58$ nm, and a wavelength spread of $\Delta\lambda/\lambda = 0.1$ was used. A weak magnetic field (1 mT) guiding the polarization was applied horizontally and perpendicularly to the incident neutron beam. It is well known that $Mn_{1-x}Fe_xSi$ orders below T_c in a helical spin structure with a small propagation vector $0.36 < k < 0.8$ nm^{-1} in the concentration range $0 < x < 0.15$.[8–12] The critical temperature T_c decreases linearly for $Mn_{1-x}Fe_xSi$ compounds upon increase in x from $T_c \approx 29$ K for pure MnSi to $T_c \rightarrow 0$ for $x \rightarrow 0.15$.[11,12] The magnetic chirality γ_m was determined in the ordered helix phase, i.e., for crystals with a critical temperature T_c which was higher than 4 K. The γ_m ratio for these samples was established to be equal to $\pm 1.00(1)$ and shows no change in the whole temperature range $T < T_c$ for the individual sample. This behavior signifies that, similar to synchrotron diffraction experiment, we have studied single-domain and enantiopure crystals.

The magnetic chirality γ_m is given in Table I. The magnetic system of most of the crystals shows left-handed helicity (LHH) and only two crystals at ($x=0$ and $x=0.10$) possess the right-handed helix. Here we emphasize on the coupling of the helix chirality to the crystallographic handedness: the left-handed helix corresponds to the left-handed crystal and vice versa. This is opposite to what has been recently found for the $Fe_{1-x}Co_xSi$ system, where left-handed crystals match the right-handed magnetic helix and the other way around.[3] We have to stress that the observed relationship for crystal and magnetic chiralities for both $Fe_{1-x}Co_xSi$ (Ref. 3) and $Mn_{1-x}Fe_xSi$ series has been established according to the identical experimental protocols. Crystal quality, sample preparation, scattering experiments, and data analysis were kept the same or as close as possible for both series of compounds to minimize possible errors and to strengthen the direct comparison; this care on experimental procedure sup-

ports our experimental findings that call therefore for a theoretical understanding. According to theoretical analysis[13] right-handed crystal structure should correspond to right-handed magnetic helix and to the negative sign of DM interaction; the same holds for left-handed crystal structure in combination with left-handed helix.[1] It is, therefore, clear that two types of the compounds, Mn and Fe based, possess different signs of the DM interaction responsible for their spiral structures.[14,15]

While the sign of DM interaction is a function of the ratio of structural and magnetic chiralities, the strength of the DM interaction $\langle S \rangle D$ is determined mostly by the value of the interacting spins. It is bigger for MnSi (≈ 0.4 μ_B per atom) than for $Fe_{1-x}Co_xSi$ compounds (≈ 0.25 μ_B per atom being maximal for $x=0.35$).[16,17] The value of the DM constant, as shown in Ref. 2, is the same for all these compounds of both types and is equal to $|D| \approx 1.1$ μ_B/a meV. This is related to the fact that the constant $|D|$ is determined by the type of the noncentrosymmetric structure ($P2_13$) and the lattice constant a, which is almost the same for all these compounds.

The change in the ratio between the structural and magnetic chiralities of the metal sublattice in combination with the corresponding change in sign of the DM constant led us to inspect other properties of Mn- and Fe-based silicides that show opposite behavior for the two series. As an example the magnetoresistance (MR) is negative for MnSi but positive for $Fe_{1-x}Co_xSi$.[17,18] The absence of the anomalous Hall effect in MnSi and significant anomalous Hall effect in $Fe_{1-x}Co_xSi$ is yet another illustration of different behavior for two seemingly similar compounds.

Taken together, these findings agree with a relative localization of magnetic density in Mn series and presumably itinerant character of magnetism in Fe-based compounds.[16,17] We propose to parametrize the correlation between the structural and magnetic chiralities and the magnetoresistance within the following empirical rule: the product of the crystal handedness, the helix chirality, and the sign of the magnetoresistive effect in the system should be negative $[\Gamma_c \gamma_m \text{sgn}(MR) < 0]$ (see Table I for the sign definition). Furthermore, one can speculate that such a product could be considered as an additional coupling of the lattice and the magnetic and electronic systems resembling a multiferroic effect. However, the observed correlation between structural handedness, chirality of magnetic structure, and transport properties presents a different type of structure-property relation. The necessary symmetry conditions for this effect are crystal class without symmetry element of the second kind such as mirror and glide planes and/or rotoinversion axis in combination with DM interaction. We do not suggest yet the underlying mechanism of this relation; there could be a similarity with chiral processes accompanying scattering of conducting electrons on localized f electrons.[19]

We conclude with a note on a control of chirality of magnetic structures. A torsion deformation has been used to change population of left and right spirals in metallic Ho.[20] A similar effect can be achieved when crossed electric and magnetic fields are applied during cooling of dielectric $ZnCr_2Se_4$.[21] For metal silicides considered here such an effect is not possible due to the strong interplay between structural and magnetic chiralities. However, the correlation of

chiral and transport properties suggests a different way of tuning magnetic chirality. The transport properties of metal silicides can be affected by chemical doping as it has been recently demonstrated for $FeSi_{1-x}Ge_x$.[22] This system is, therefore, an attractive candidate to probe a switch of the sign of DM interaction as function of the Ge concentration. Such a switch would open a possibility to control the sense

of magnetic chiral structures in cubic magnets with DM interaction. Further experimental and theoretical studies should find whether such a control is possible.

[1] M. Tanaka, H. Takayoshi, M. Ishida, and Ya. Endoh, J. Phys. Soc. Jpn. **54**, 2970 (1985); M. Ishida, Ya. Endoh, S. Mitsuda, Y. Ishikawa, and M. Tanaka, *ibid.* **54**, 2975 (1985).

[2] C. Viedma, Phys. Rev. Lett. **94**, 065504 (2005).

[3] 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).

[4] H. D. Flack, Acta Crystallogr., Sect. A: Found. Crystallogr. **39**, 876 (1983).

[5] H. D. Flack, Acta Crystallogr. A **55**, 908 (1999).

[6] S. V. Maleyev, Phys. Rev. Lett. **75**, 4682 (1995).

[7] V. E. Dmitrienko, Acta Crystallogr. A **50**, 515 (1994).

[8] Y. Ishikawa, K. Tajima, D. Bloch, and M. Roth, Solid State Commun. **19**, 525 (1976).

[9] Y. Ishikawa, G. Shirane, J. A. Tarvin, and M. Kohgi, Phys. Rev. B **16**, 4956 (1977).

[10] G. Shirane, R. Cowley, C. Majkrzak, J. B. Sokoloff, B. Pagonis, C. H. Perry, and Y. Ishikawa, Phys. Rev. B **28**, 6251 (1983).

[11] Y. Nishihara, S. Waki, and S. Ogawa, Phys. Rev. B **30**, 32 (1984).

[12] 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).

[13] M. Kataoka, O. Nakanishi, A. Yanase, and J. Kanamori, J. Phys. Soc. Jpn. **53**, 3624 (1984).

[14] I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. **46**, 1420 (1964).

[15] P. Bak and M. H. Jensen, J. Phys. C **13**, L881 (1980).

[16] N. Manyala, Y. Sidis, J. F. DiTusa, G. Aeppli, D. P. Young, and Z. Fisk, Nature (London) **404**, 581 (2000).

[17] N. Manyala, Y. Sidis, J. F. DiTusa, G. Aeppli, D. P. Young, and Z. Fisk, Nature Mater. **3**, 255 (2004).

[18] C. Pfleiderer, S. R. Julian, and G. G. Lonzarich, Nature (London) **414**, 427 (2001).

[19] J. Kondo, Prog. Theor. Phys. **27**, 772 (1962); S. V. Maleev, Phys. Usp. **45**, 569 (2002).

[20] V. I. Fedorov, A. G. Gukasov, V. Kozlov, S. V. Maleyev, V. P. Plakhty, and I. A. Zobkalo, Phys. Lett. A **224**, 372 (1997).

[21] K. Siratori, J. Akimitsu, E. Kita, and M. Nishi, J. Phys. Soc. Jpn. **48**, 1111 (1980).

[22] S. Yeo, S. Nakatsuji, A. D. Bianchi, P. Schlottmann, Z. Fisk, L. Balicas, P. A. Stampe, and R. J. Kennedy, Phys. Rev. Lett. **91**, 046401 (2003).