

Control of chirality of transition-metal monosilicides by the Czochralski methodV. A. Dyadkin,¹ S. V. Grigoriev,^{1,*} D. Menzel,² D. Chernyshov,³ V. Dmitriev,³ J. Schoenes,² S. V. Maleyev,¹ E. V. Moskvina,¹ and H. Eckerlebe⁴¹*Petersburg Nuclear Physics Institute, Gatchina, RU-188300 St. Petersburg, Russia*²*Institut für Physik der Kondensierten Materie, Technische Universität Braunschweig, D-38106 Braunschweig, Germany*³*Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility, Grenoble F-38000, France*⁴*Gesellschaft für Kernenergieverwertung in Schiffbau und Schifffahrt Forschungszentrum, D-21502 Geesthacht, Germany*

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The crystallographic and magnetic chirality of the B20 (space group $P2_13$) solid solutions $Fe_{1-x}Co_xSi$ and pure MnSi grown by the Czochralski method has been studied by means of the single crystal x-ray diffraction and the small-angle diffraction of polarized neutrons. To test the possibilities to control the crystal handedness, first, we have grown a series of MnSi crystals and one series of $Fe_{1-x}Co_xSi$ samples with $x = 0, 0.10, 0.15, 0.20, 0.25, 0.30, 0.50$ using a right-handed crystal as a seed. Second, we have grown another series of MnSi and $Fe_{1-x}Co_xSi$ samples again of different concentrations using a left-handed crystal as a seed. In 90% of the cases the grown sample has been found to be enantiopure and to inherit the crystallographic chirality of its seed crystal. In 10% of the cases undefined circumstances flip the chirality over for the next progeny or produce a racemic sample. The magnetic chirality of these compounds has been shown to be rigorously related to their crystallographic handedness, but in the opposite way for MnSi and for $Fe_{1-x}Co_xSi$.

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I. INTRODUCTION

Chirality (or handedness), which is defined as the difference between left and right mirror images appears as one of the inalienable properties of our universe. The principal manifestation of the handedness in condensed matter physics is the broken inverse symmetry of some types of crystals. The symmetry group of these crystals must be restricted to nonmirror or noninversion symmetry operations and the operations $\bar{1}$, m , $\bar{3}$, 4 , 6 are abandoned. In other words, the crystal is chiral because it is not superposable by pure rotation or translation with its mirror image generated by the point inversion. Crystalline quartz serves as an example of such chiral crystals because it exists in either right- (space group $P3_121$) or left-handed (space group $P3_221$) enantiomorphs.¹

The absolute majority of the transition-metal monosilicides (TMMSs) such as MnSi, FeSi, CoSi and their solid solutions also crystallize in the chiral space group $P2_13$ (structure B20),² which can exist in both left- and right-handed enantiomorphs. This chiral structure forces TMMSs to become chiral magnets (i.e., they are magnetically ordered in a spin helical structure with the rather long period of 10–100 nm).^{3–9} The spin helicity is a result of the equilibrium between the ferromagnetic exchange interaction and the antisymmetric Dzyaloshinskii-Moriya (DM) interaction caused by the lack of an inversion symmetry in the atomic arrangement.^{10–12} A weak anisotropic exchange (AE) interaction tends to fix the direction of the helix along the principal cube directions: either $\langle 111 \rangle$ or $\langle 100 \rangle$ axes.¹¹

The problem of the TMMS chirality was reported in the middle of the 1980s when seven MnSi and three $Fe_{1-x}Co_xSi$ crystals with $x = 0.20, 0.40$ and 0.50 were found to be structurally left-handed for all samples.^{5,13} The concomitant spin helix chirality of these MnSi samples was also left-handed^{5,14} but it was right-handed for $Fe_{1-x}Co_xSi$ compounds.⁵ In spite of the fact that the authors of the paper⁵ did not make any far-reaching conclusions and even forewarned that the

selection is inadequately representative, these results had created a conviction among the some experts that MnSi-related compounds may exist as the left-handed enantiomorphs only (the broken chiral symmetry paradigm).

The fact that compounds with the space group $P2_13$ can form either left or right enantiomorphs was repeatedly proved. For example, the inorganic physicochemical crystallization process of sodium chlorate $NaClO_3$ (B20 structure) had become a classical archetype for spontaneous homochirality.¹⁵ Starting from an undisturbed supersaturated solution one observes that statistically equal numbers of levorotary and dextrorotary crystal nuclei are created. The presence of a small enantiomeric excess of 5% in the precursor results in 100% homochirality within eight hours in specific multistage autocatalytic reaction systems.¹⁶ Moreover, a homochiral batch of $NaClO_3$ crystals can be produced even in a one-step reaction with an initial enantiomeric excess of $10^{-7}\%$.¹⁷ Since the final chirality can be either 100% left-handed or 100% right-handed with the probability of 50%, all these experiments prove that the chiral handedness in $NaClO_3$ crystals is energetically degenerated.

Thus, from an energetic point of view it seemed quite puzzling why nature should create only left-handed crystals in the TMMS case and both kinds of chiral enantiomorphs in the $NaClO_3$ case. The lack of research attention to this puzzle of the broken chiral symmetry in TMMSs may be linked to the following. Firstly, due to the high crystallization temperatures (more than 1700 K) single crystals of TMMS are not easy to grow. Secondly, the chirality of TMMS is impossible to measure using polarized light as it is routinely performed for $NaClO_3$. As in our previous work¹⁸ we have used two different techniques to define the crystallographic handedness and the magnetic chirality. The absolute structure and its chiral configuration were determined by properly collected single-crystal x-ray diffraction data, and the magnetic chirality can be characterized using polarized small-angle neutron scattering.

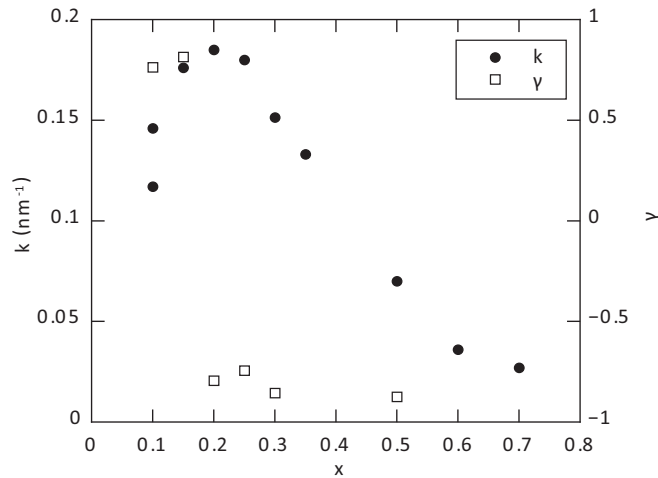


FIG. 1. Dependence of the helix wave vector k and the chirality γ on the Co concentration x for $\text{Fe}_{1-x}\text{Co}_x\text{Si}$.

In our previous study¹⁸ we investigated high-purity single crystals of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ with $x = 0.1, 0.15, 0.20, 0.25, 0.30$, and 0.50 grown by the Czochralski method. We showed that the compounds with $x = 0.08, 0.1, 0.15$ are crystallographically right handed while the compounds with $x = 0.2, 0.25, 0.30, 0.50$ are crystallographically left handed. At the same time the magnetic chirality is flipped with respect to the crystallographic handedness for all these samples. The results of the study seemed to confirm the findings of the early investigations.^{5,13} Being within the broken chiral symmetry paradigm we suggested that chirality might depend on the Co concentration x . This hypothesis is supported by the rather unusual behavior of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ in the range $0.20 \leq x \leq 0.30$ where several key parameters exhibit well-defined maxima. One of such parameters is the critical temperature T_C .^{19,20} Another one is the wave vector $|\mathbf{k}|$, which defines the period of the spin helix as $d = 2\pi/k$. The concentration dependence of $|\mathbf{k}|$ along with the magnetic chirality γ is presented in Fig. 1. It demonstrates a maximum close to $x = 0.20$ together with the flip of the magnetic chirality, which is correlated to the crystallographic handedness.

Thus, the obtained results might be well expected within the frame of the broken chiral symmetry paradigm. To finally test the possibility to control the crystal handedness of TMMS single crystals we have proposed to perform the following experiments with the crystal growth using the tri-arc Czochralski technique. (i) Using a right-handed crystal with $x = 0.10$ (from the left side of Fig. 1) as a seed we have grown one series of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ samples with $x = 0.10, 0.15, 0.20, 0.25, 0.30, 0.50$. (ii) Using a left-handed crystal with $x = 0.50$ (from the right side of Fig. 1) as a seed we have grown another series of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ samples again of different concentrations. The result of these experiments aims to demonstrate whether the handedness of TMMSs depends on the concentration of Co or is solely determined by the seed used for this synthesis. The third option could be that the handedness would not depend on the seed and/or the concentration x .

The same two seeds were exploited in order to test the hypothesis of the broken chiral symmetry paradigm with respect to pure MnSi crystals. We grow two series of MnSi,

three pieces each, from the seeds of opposite chiralities. Going ahead with the conclusions, we have experimentally proven that the MnSi and the $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ species exist in both the left- and right-handed configuration and in most cases it is a seed crystal that transfers the chirality to the newly grown crystal.

II. CRYSTALLOGRAPHIC STRUCTURE AND ITS CHIRALITY

According to Tanaka *et al.*^{5,13} the solid solutions $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ and pure MnSi belong to the B20 structure type, which is identified by the space group $P2_13$ (no. 198). Assembly of atoms in the B20 structure are situated in the following Wyckoff positions:

$$4(a): R_1(u, u, u); \quad R_2\left(\frac{1}{2} + u, \frac{1}{2} - u, -u\right); \quad (1)$$

$$R_3\left(-u, \frac{1}{2} + u, \frac{1}{2} - u\right); \quad R_4\left(\frac{1}{2} - u, -u, \frac{1}{2} + u\right)$$

It is worth noting that in literature one finds different numberings for the positions ($R_1 - R_4$). In order to provide a unifying reference we use hereafter a standard setting from the International Tables for Crystallography.²¹

Since the determination of the crystallographic chirality of this structure is not an easy concept, we give its detailed description below. Following the definition of the authors of Refs. [5,13] the right-handed structure is referred as to the one with $u_{\text{Si}} = 0.154$ and $u_{\text{Me}} = 0.865$, where Me denotes the transition metals Mn, Fe, or Co.

For the description of the left-handed structure one has to use the representation given in Eq. (1) but with different u values defined as

$$u_{\text{Me}}^L = 1 - u_{\text{Me}}^R, \quad u_{\text{Si}}^L = 1 - u_{\text{Si}}^R. \quad (2)$$

Here the superscript indexes R and L denote the right- and left-handed structures, respectively, taken on historical reason (see below). After the substitution of Eq. (2) into Eq. (1) one has to reduce the obtained values to get the atom's coordinates within the same unit cell. Finally, for the left-handed structure the atoms are situated in the following Wyckoff positions:

$$4(a): R_1(1 - u, 1 - u, 1 - u); \quad R_2\left(\frac{1}{2} - u, \frac{1}{2} + u, u\right); \quad (3)$$

$$R_3\left(u, \frac{1}{2} - u, \frac{1}{2} + u\right); \quad R_4\left(\frac{1}{2} + u, u, \frac{1}{2} - u\right)$$

with the same $u_{\text{Si}} = 0.154$ and $u_{\text{Me}} = 0.865$. Generally speaking, the operation in Eq. (2) is absolutely equivalent to the inversion operation $(x, y, z) \rightarrow (-x, -y, -z)$, which is the definition for the transformation from the right-handed to the left-handed structure and vice versa.

The definition of the right-handed and left-handed structures given by Eqs. (1) and (3) with the same numbers $u_{\text{Si}} = 0.154$ and $u_{\text{Me}} = 0.865$ is equivalent to the definition Eq. (1) with the different numbers $u_{\text{Si}}^R = 0.154$ and $u_{\text{Me}}^R = 0.865$ for the right-handed structure and $u_{\text{Si}}^L = 0.846$ and $u_{\text{Me}}^L = 0.135$ for the left-handed structure related to each other by Eq. (2). We use hereafter the latter definition.

The x-ray single-crystal diffraction was used to determine the absolute positions of the atoms in the unit cell and, as a result, the structural handedness. As was shown in Ref. 18 the structure of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ with $x = 0.25$ is indeed identified

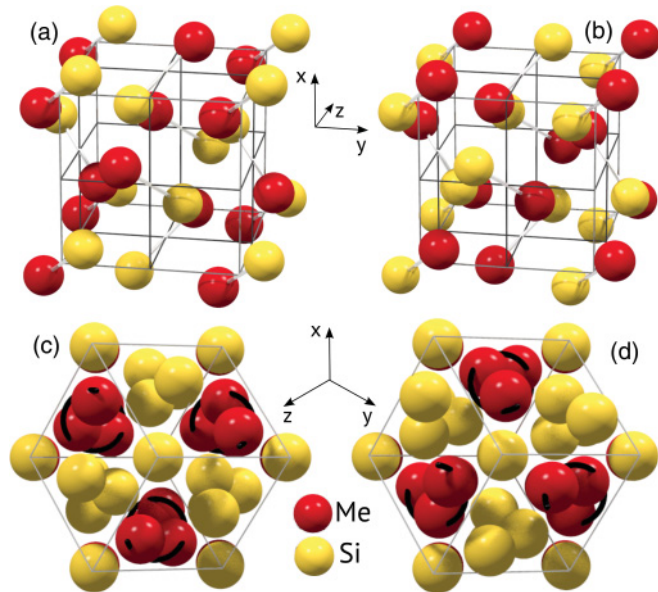


FIG. 2. (Color online) View of a B20 cubic crystal (space group $P2_13$) along the $\langle 001 \rangle$ (a), (b) and $\langle 111 \rangle$ (c), (d) axes for two chiral configurations: (a), (c) right-handed with $u_{\text{Si}} = 0.164$ and $u_{\text{Me}} = 0.862$ and (b), (d) left-handed with $u_{\text{Si}} = 0.846$ and $u_{\text{Me}} = 0.138$ [here u is the parameter in expression Eq. (1)]. The black spirals help to identify the sense of the skewing.

as B20 (space group $P2_13$) with the structural parameters $u_{\text{Fe/Co}} = 0.138$ and $u_{\text{Si}} = 0.846$ in the positions given by Eq. (1) in full correspondence with Refs. 5 and 13. Opposite to this for the compounds with $x = 0.08$ and 0.10 we had found that the structural parameters $u_{\text{Fe/Co}} = 0.865$ and $u_{\text{Si}} = 0.155$ in the positions corresponding to Eq. (1) as well. According to the definition given above the compound with $x = 0.25$ should be recognized as being left handed, while the other two compounds with $x = 0.08$ and 0.10 are structurally right handed.

The sketches in Figs. 2(a) and 2(b) show the right-handed ($x = 0.10$) and left-handed ($x = 0.25$) $P2_13$ structures where a structural motif is the Me-Si pair. These unit cells can be easily imagined by setting the Me-Si pairs into the fcc lattice sites but orienting these motifs along four $\langle 111 \rangle$ axes at four different sites $[000]$, $[0.5, 0.5, 0]$, $[0.5, 0, 0.5]$, and $[0, 0.5, 0.5]$. With the knowledge of the absolute structure the crystallographic chirality of a helix propagating along a given direction can easily be visualized by swinging this structure and scrutinizing its sight along the $\langle 111 \rangle$ axes. Figures 2(c) and 2(d) show the projection of the B20 structure along the $\langle 111 \rangle$ axis. The Si atoms forming a helix (not lying on the $\langle 111 \rangle$ axis) are skewing around it in the certain right-handed configuration for $x = 0.10$ and in the left-handed configuration for $x = 0.25$. The Me atoms form a similar but right-handed helix along $\langle 111 \rangle$ (a), in accordance to its parameter $u_{\text{Me}} = 0.862$, and a left-handed configuration for $u_{\text{Me}} = 0.138$ (b). Thus, by this definition the chirality of the whole structure coincides with the chirality of the silicon sublattice. It should be noted that the views shown in Figs. 2(c) and 2(d) are the same along all four $\langle 111 \rangle$ axes.

III. METHODS

The methods applied to determine absolute (chiral) structural and spin configurations are described in our previous work.¹⁸ The absolute crystal structure can be established by the x-ray single-crystal diffraction data providing that resonant contribution enables to observe violation of Friedel's law, a complete methodology can be found in Refs. 22 and 23. For MnSi and isostructural compounds the handedness of the absolute structure is defined for a chiral structural construction; in our case this is simply a sense of a spiral propagating along $\langle 111 \rangle$ and built from Si ions. For a helical magnetic structure absolute configuration is defined by the sense of corresponding magnetic spiral. Methodology of experimental determination of the magnetic chirality with small-angle neutron diffraction has been shown in Ref. 18 (see also Ref. 24). If the crystal under study is a mixture of two types of domains of opposite chirality, a fraction of domains with given absolute crystal or magnetic structure is also refined from the diffraction data; for x-ray diffraction this fraction is called the Flack parameter, for polarized neutron diffraction it is the magnetic chirality.

The x-ray diffraction measurements were performed with synchrotron radiation with $\lambda = 0.77 \text{ \AA}$ at the Swiss-Norwegian Beam Line BM1A at the European Synchrotron Radiation Facility (ESRF) using the KUMA6 diffractometer. Crystals with an average size of about 50 microns were cut from the large single crystals synthesized for these experiments. The polarized small-angle neutron scattering was measured with the help of the SANS2 instrument at the Geesthacht Neutron Facility (GeNF). The magnetic chirality γ was determined below T_C (i.e., in the ordered helix phase).

IV. CRYSTAL GROWTH

To check the hypothesis whether the crystal handedness depends on the Co concentration or is determined by the seed, we have grown a series of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ single crystals using samples with $x = 0.08$ and $x = 0.10$ as right-handed seeds and one sample with $x = 0.25$ as a left-handed seed. To prove the possibility of the existence of right-handed MnSi crystals we have also grown manganese silicides using $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ crystals with $x = 0.08$ and $x = 0.25$ as right- and left-handed seeds, respectively. This growth appears to be possible due to the same crystal structure and very similar cubic lattice parameter of the seeds and the resulting crystals. For the tri-arc Czochralski crystal growth high-purity components were mixed stoichiometrically and molten in a water-cooled copper crucible under argon atmosphere with a pressure of 0.6 bar and 2.5 bar for $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ and MnSi crystals, respectively. The heating was provided by three electric arcs. The clockwise revolving seed crystal was submerged into the reversely rotating melt. Subsequently, the crystal was slowly drawn out of the melt with the speed of 12 mm/h. It should be noticed that the growth conditions were the same for all $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ and MnSi crystals (excluding argon pressure which was five times larger for MnSi due to the huge vapor pressure of liquid manganese).

A. $\text{Fe}_{1-x}\text{Co}_x\text{Si}$

As initial seeds we took well-defined crystals from the first set with $x = 0.08$ and 0.25 , which were determined

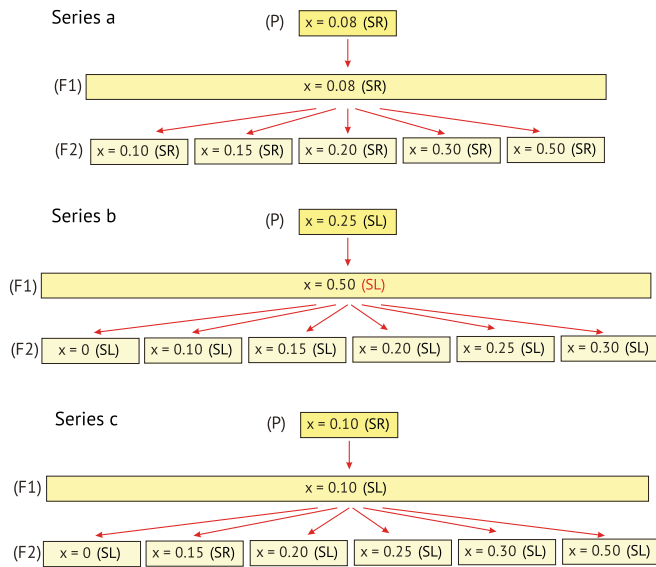


FIG. 3. (Color online) $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ samples grown from the right-handed (P) seed (series a), from the left-handed (P) seed (series b), and from another right-handed (P) seed (series c). The structural handedness determined in the experiment is denoted as (SR) for right-handed crystals and as (SL) for left handed crystals.

as structurally right- and left-handed, respectively. They are denoted in Figs. 3(a) and 3(b) as the parental generation (P). Further, we have grown the second-generation crystals (F1) with the Co concentrations $x = 0.08$, and 0.50 [Figs. 3(a) and 3(b), respectively]. We suggested that if the crystal handedness can be inherited from the (P) crystal to the (F1) crystal then we produce the crystal of the same handedness long enough (10–15 cm) to be cut and serve as a seed for many other crystals of the next generation denoted (F2) in Fig. 3.

Using the (F1) sample of series 1 as a seed, the other five (F2) samples with $x = 0.10, 0.15, 0.20, 0.30$, and 0.50 were grown. The x-ray experiments revealed that all (F2) samples are structurally right-handed, the same as for the (F1) and the initial (P)-seed crystals. The polarized neutron scattering experiments had shown that all crystals of this series produce left-handed spin helices below the ordering temperature T_c .

The second series [Fig. 3(b)] shows the similar behavior: The (F1) and all (F2) crystals with $x = 0, 0.10, 0.15, 0.20, 0.25$, and 0.30 have inherited the left structural handedness from their (P)-seed crystal. All these crystals were determined to have the right magnetic chirality. Naturally, the pure FeSi crystal inherited the left handedness but it is not magnetically ordered. It is worthy to note that all samples under investigation show perfect crystallographic structure.

The curious example of a hoax, which nature can play on us, is a third series of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ with $x = 0, 0.10, 0.15, 0.20, 0.25, 0.30$, and 0.50 [Fig. 3(c)]. The (P) seed was a right-handed crystal with $x = 0.10$. The (F1) crystal of the same concentration $x = 0.10$ was grown as a long crystal (of 10 cm) to be used as a seed for other crystals. When the other (F2) samples were also grown, the inspection of their handedness has shown that (F1) crystal and most of the (F2) crystals are left handed, except for one with $x = 0.15$, which was again right handed. The very first impression could be that the right-handed crystal (P) seed produces preferably the

left-handed crystals in (F1) and (F2) generations. In reality, the handedness has been accidentally flipped upon the growth of the (F1) sample. Afterward, almost all (F2) crystals had inherited the handedness from their (F1) seeds.

Thus, the whole three series of experiments have clearly shown that the Czochralski technique produces in most cases the crystals of the same handedness as that of the seed. Additionally, careful inspection of the (F2) crystals from the first and second series revealed that $\text{Fe}_{0.50}\text{Co}_{0.50}\text{Si}$ from series (a) and $\text{Fe}_{0.80}\text{Co}_{0.20}\text{Si}$, $\text{Fe}_{0.75}\text{Co}_{0.25}\text{Si}$ from series (b) are racemic with 20% contribution of the opposite chiral domains in its crystallographic as well as magnetic realizations. Obviously, the chiral heredity is sometimes interrupted, and certain unintentional circumstances during the growth process can flip over the handedness of the growing crystal.

B. MnSi

Since MnSi and $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ have the same crystal structure and close lattice parameters, it is possible to grow MnSi using a $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ seed crystal (Fig. 4). Two MnSi series, which consist both of three (F2) crystals, inherited the structural chirality of their parent (F1) $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ crystals. Three left-handed crystals of MnSi were obtained in the first series [Fig. 4(a)]. Only two right-handed (F2) MnSi crystals were obtained in the second series [Fig. 4(b)]. One crystal of this series appeared to be racemic (i.e., partially right handed and partially left handed). Thus one concludes that the MnSi crystals grown by the Czochralski method have inherited the handedness of their seeds but sometimes, probably due to the creation of defects during the crystallization process, the

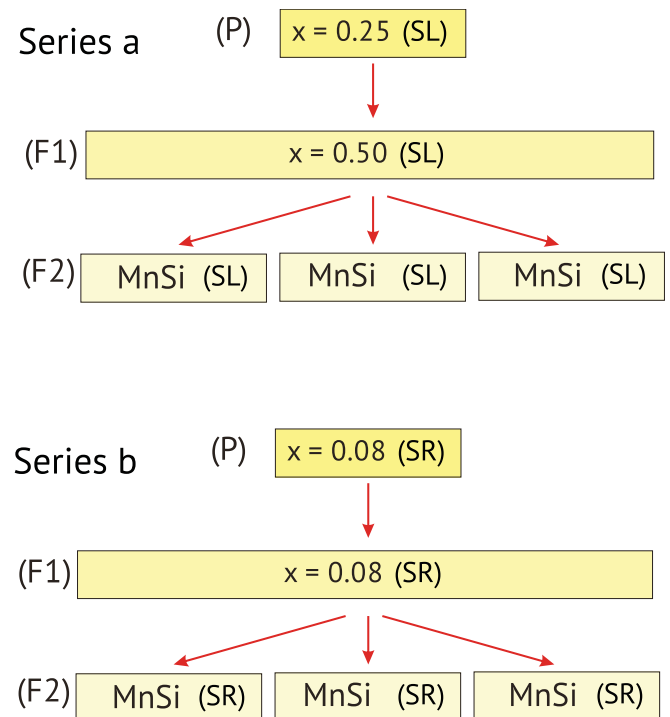


FIG. 4. (Color online) Series of the MnSi samples grown from the left-handed (P) seed (series a) and from the right-handed (P) seed (series b).

handedness is flipped in the whole sample or in its part, thus producing a racemic sample.

One can conclude on the basis of our experiments that the observation of Tanaka *et al.*,^{5,13} concerning seven left-handed Czochralski-grown MnSi crystals, is most likely based on the fact that all these specimens originated from the same seed crystal or from the seeds of the same chirality.

V. CONCLUSION

In summary, using x-ray single-crystal diffraction and polarized neutron scattering we measured the crystal handedness and the spin helix chirality of three series of Fe_{1-x}Co_xSi crystals and two series of MnSi crystals. We conclude that the handedness of Fe_{1-x}Co_xSi crystals does not depend on the Co concentration, but it is determined by the seed's handedness, which can thus be called an inherited parameter. We have also shown that MnSi crystals can be realized as both left-handed and right-handed enantiomorphs. Although some uncontrolled circumstances are able to flip the handedness, the heredity of the handedness generally offers the possibility to control it and enables one to intentionally grow samples of the desired handedness.

We have also proved that the structurally left-handed samples of Fe_{1-x}Co_xSi (with $u_{\text{Me}} = 0.138$, $u_{\text{Si}} = 0.846$) drive right-handed spin helices and, conversely, crystallographically right-handed samples (with $u_{\text{Me}} = 0.862$, $u_{\text{Si}} = 0.155$) show left-handed helices. This situation is opposite in the case of MnSi where a left-handed crystal generates the left-handed magnetic spirals and vice versa. These two types of compounds obviously possess different signs [negative sign (–) for MnSi and positive sign (+) for Fe_{1-x}Co_xSi] of the Dzyaloshinskii-Moria interaction that determines their spiral structure.¹¹

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