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# Chromium and iron contained half-Heusler MnNiGe-based alloys

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The magnetic characteristics of chromium and iron containing MnNiGe-based alloys with several types of quenching and annealing were investigated. It was found that the quenched $Mn_{0.89}Cr_{0.11}NiGe$ has a spontaneous and magnetic field induced magnetostructural first-order transitions at room temperature. These transitions might be accompanied by a large magnetocaloric effect. In general, $Mn_{0.89}Cr_{0.11}NiGe$ can be classified as promising material for use in the magnetocaloric application at room temperatures. The first order magnetostructural phase transition from the ferromagnetic to paramagnetic state is not realized in MnNi0.90Fe0.10Ge. In contrast to $Mn_{0.89}Cr_{0.11}NiGe$, however, the FM state in quenched-on-wheel MnNi0.90Fe0.10Ge is preserved to the lowest temperatures. Based on the set of the magnetic properties, it has been concluded that the iron containing MnNiGe-based alloys are less promising for practical use. Q2 Q3



## 1. Introduction

There is a large group of half-Heusler alloys based on MnNiGe, MnCoGe and MnCoSi ternary compounds, where magnetostructural phase transitions are occurs. The strong correlation between the magnetic and lattice subsystems in these materials is very important for both fundamental science and practical application. Namely, they are magnetostriction, magnetoresistance, giant magnetocaloric effect induced by the magnetic field, the magnetic shape memory effect. The particularly important for practical applications is to obtain the selection of suitable doping in ternary alloys MnNiGe, MnCoGe, MnCoSi that can implement new magnetostructural sequence of phase transitions [1–3].

The aim of this work is to compare the magnetic properties and phase transition characteristics of MnNiGe based alloys with additions of (1) iron and (2) chromium.

At high temperatures MnNiGe is the paramagnetic compound with the hexagonal crystal structure of $Ni_2In$-type (symmetry group $P6_3/mmc$) [4].When temperature is lowered to $T_t = 470$ K the diffusionless structural transformation occurs to a low-temperature martensitic orthorhombic structure of TiNiSi-type (symmetry group $P_{nma}$). At further decrease in temperature, the isostructural magnetic phase transition from paramagnetic (PM) to helical antiferromagnetic (AF) structure ($T_N = 346$ K) is observed.

## 2. Results and discussion

The samples considered in the paper were: (1) previously sufficiently studied $MnNi_{1-x}Fe_xGe$ [1, 5], and (2) the relatively new $Mn_{1-x}Cr_xNiGe$ [6] systems. As the fundamental changes of properties in MnNiGe-based alloys are observed even at low contents of replacement components, therefore the $Mn_{0.89}Cr_{0.11}NiGe$ and $MnNi_{0.90}Fe_{0.10}Ge$ samples have been chosen for the comparison. Both types of samples were prepared by induction melting of the elements of the initial powders, purity not less than 99.99% all in corresponding proportions. The sample $Mn_{0.89}Cr_{0.11}NiGe$ was then heat treated by two different ways: annealing at 850 °C for 6hours and (1) slowly cooled or (2) quenching from 850 °C into water. The melted $MnNi_{0.90}Fe_{0.10}Ge$ sample was pouring out on the rapidly rotating copper wheel. After such quenching one of $MnNi_{0.90}Fe_{0.10}Ge$ samples was annealed at $T = 850$ °C for 6hours and slowly cooled.

Thus, the magnetic characteristics of chromium and iron contained samples with several types of quenching and annealing were investigated.

The phase composition of the investigated samples was monitored using a diffractometer DRON-3 with Cu-Kα radiation and low-temperature X-ray camera SCC–190. In small magnetic fields

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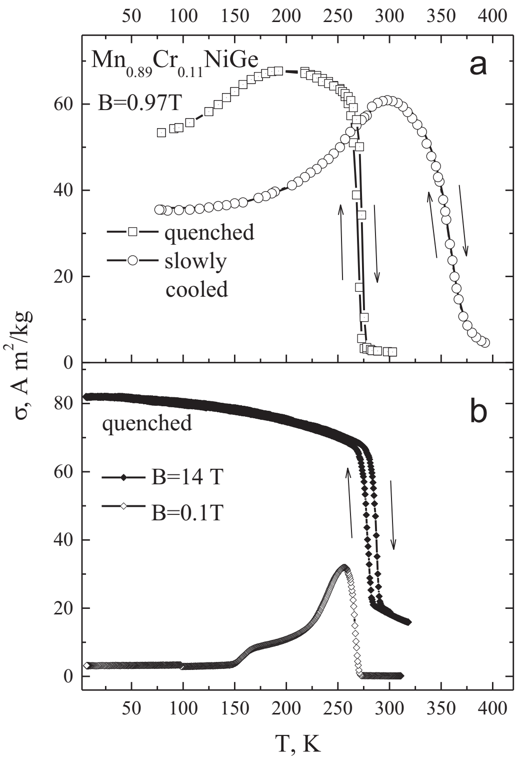


**Fig. 1.** Temperature dependences of magnetization: (a) quenched into water from 850° C (□) slowly cooled (○) $Mn_{0.89}Cr_{0.11}NiGe$ samples in the magnetic field 0.97 T; (b) quenched into water from 850° C in the magnetic fields $B=14$ T (♦) и $B=0.1$T (◇).

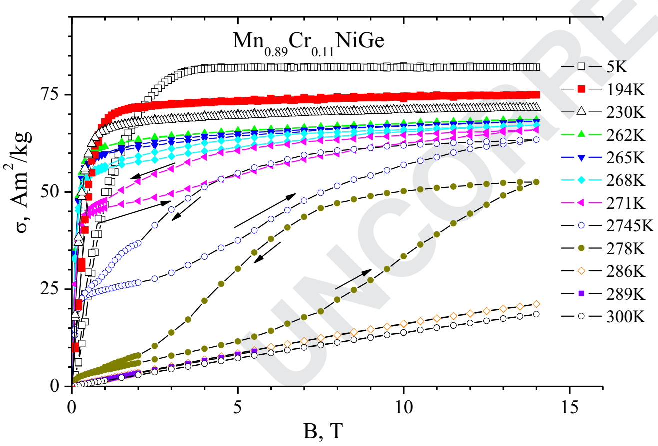


**Fig. 2.** Isothermal magnetization curves for quenched $Mn_{0.89}Cr_{0.11}NiGe$ at different temperatures.

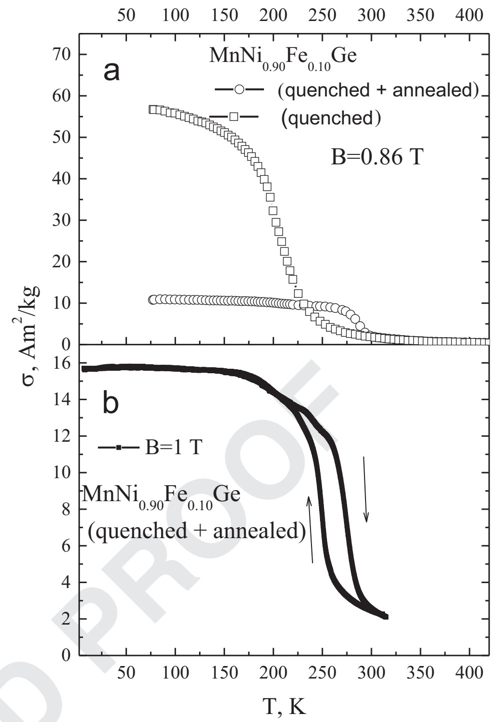


**Fig. 3.** Temperature magnetization dependences for $MnNi_{0.90}Fe_{0.10}Ge$ (quenched and quenched+annealed): (a) in the field of 0.86 T; (b) 1 T.

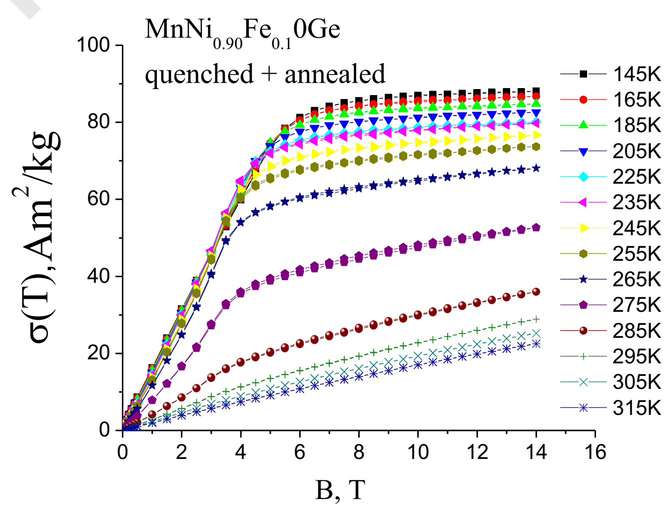


**Fig. 4.** Isothermal magnetization curves for quenched $MnNi_{0.90}Fe_{0.10}Ge$ (quenched+annealed sample) at different temperatures.

($B<1$ T) the temperature and field dependences of the magnetization were measured by Domenicali pendulum magnetometer, in the fields $B<14$ T – by the vibration magnetometer of Cryogenic Limited. Curie temperatures were determined by the extrapolation of the linear part of the temperature dependence of specific magnetization square curve to the temperature axis.

Chromium containing slowly cooled sample $Mn_{0.89}Cr_{0.11}NiGe$ has a hexagonal $Ni_2In$-type crystal structure above and below the magnetic disordering temperature $T_C\sim360$ K. The isostructural FM–PM magnetic phase transition is smooth, temperature stretch and magnetization value has no temperature hysteresis (Fig. 1a).

Quenching of the $Mn_{0.89}Cr_{0.11}NiGe$ enhances the stability region of PM hexagonal phase towards low temperatures. This type of treatment also changes the nature of the magnetic ordering in $Mn_{0.89}Cr_{0.11}NiGe$ from the isostructural hysteresis-free second-order phase transition ($T_C\sim360$ K) to the magnetostructural first-order phase transition ($T_C\sim275$ K). This first-order phase transition is accompanied by significant temperature hysteresis of magnetization value (Fig. 1), the sharp change in the lattice parameters [6]. At the same time the phase composition of the sample is changing from almost single-phase hexagonal $Ni_2In$ structure in the paramagnetic state to the two-phase (20% hexagonal $Ni_2In$ and 80% orthorhombic TiNiSi phases) in the ferromagnetic state [6]. The magnetic measurements in the weak magnetic field 0.1 T (Fig. 1b) show that only in a narrow temperature range 275–250 K the stable FM order in $Mn_{0.89}Cr_{0.11}NiGe$ has place. In the temperature range from 250 K to 150 K the superposition of AF–FM states appears, and below 150 K one can talk about pure AF state. It is confirmed by isothermal magnetization curves $\sigma(B)$ of quenched sample $Mn_{0.89}Cr_{0.11}NiGe$ (Fig. 2). As it is seen from Fig. 2, the

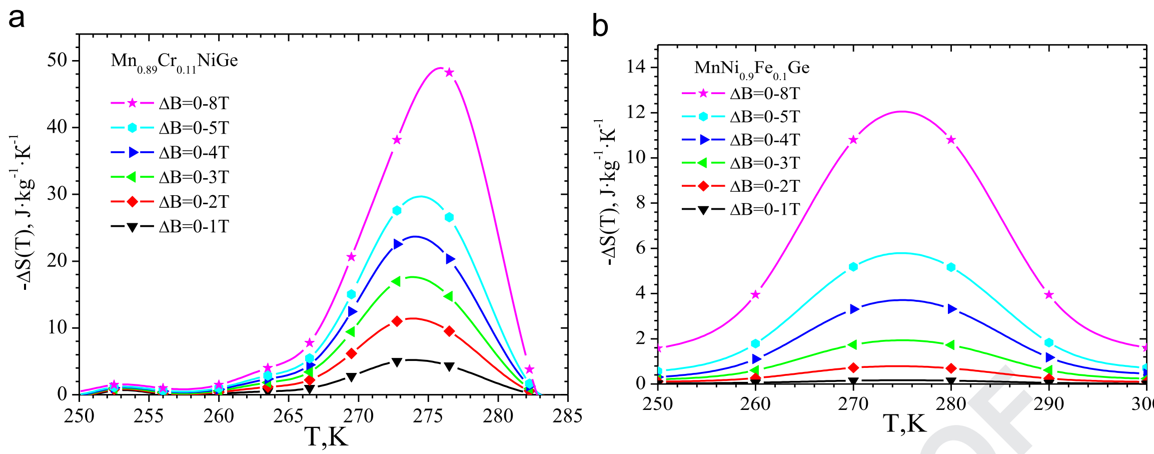


**Fig. 5.** The temperature dependence of $-\Delta S$ for quenched $Mn_{0.89}Cr_{0.11}NiGe$ (a) and quenched+annealed $MnNi_{0.9}Fe_{0.1}Ge$ (b).

saturation of the low-temperature field magnetization dependence (at $T=5$ K) is achieved only at $B=3$ T, that can be interpreted as a smooth field induced transition from AF to FM state.

When Ni in MnNiGe is replaced by Cr, the emergence of FM phase has place by isostructural magnetic phase transition [7]. However, unlike to $Mn_{1-x}Cr_xNiGe$ system, such kind of substitution in $MnCr_xNi_{1-x}Ge$ considerably lowers the phase transition temperature ($T_C \sim 200$ K for $MnNi_{0.895}Cr_{0.105}Ge$) and leads to emergence of metamagnetic transition of FM–AF type with $T_M \sim 125$ K and a considerable temperature hysteresis ($T=17$ K). Magneto caloric characteristics of PM–FM phase transitions in these two systems also considerably differ. The value of $-\Delta S$is 30 J/kg K for $Mn_{0.89}Cr_{0.11}NiGe$ and 5 J/kg K for $MnNi_{0.895}Cr_{0.105}Ge$ [7]. Thus, the $Mn_{1-x}Cr_xNiGe$ system is more perspective for magnetocaloric applications.

The temperature dependences of the magnetization in different magnetic fields for iron contained samples $MnNi_{0.90}Fe_{0.10}Ge$ are given in Fig. 3. X-ray analysis showed that both samples with different heat treatment have orthorhombic TiNiSi-type crystal structure before and after magnetic phase transition. The quenched sample is ferromagnetic at room temperature and the FM–PM transition temperature is $T_C=218$ K. The additionally annealed sample $MnNi_{0.90}Fe_{0.10}Ge$ (quenched+annealed) has a very low magnetization value, the temperature of its magnetic phase transition $T_N=295$ K is close to room temperature, and the temperature dependence of the magnetization $\sigma(T)$ in small fields of about 1 T exhibits hysteresis properties in the transition region and is sufficiently sharp, Fig.3b. Isothermal magnetization-field dependence (Fig. 4) of the quenched+annealed sample has a form characterized to the state without a spontaneous magnetization. From a comparison of Figs. 3 and 4 it is clear that for such treated $MnNi_{0.90}Fe_{0.10}Ge$ sample at low temperatures the saturation magnetization 80 A $m^2$/kg is realized only in the fields about 6 T.

Spontaneous FM state is realized only for quenched $MnNi_{0.90}Fe_{0.10}Ge$ sample below the Curie temperature $T_C=218$ K by means of smooth isostructural (TiNiSi) phase transition PM–FM. In quenched+annealed $MnNi_{0.90}Fe_{0.10}Ge$ at 295 K an abrupt transition is realized to a state with magnetization about 16 A $m^2$/kg in $B=1$ T. This temperature can be considered as the Neel temperature and the state in the field 1 T represents a slightly magnetized antiferromagnetic structure.

## 3. Conclusion

It was found that the type of heat treatment of $Mn_{0.89}Cr_{0.11}NiGe$ and $MnNi_{0.90}Fe_{0.10}Ge$ strongly affects the stability region of crystalline and magnetic phases and the nature of the magnetic phase transitions in these samples. The quenched $Mn_{0.89}Cr_{0.11}NiGe$ has a (i) spontaneous and (ii) magnetic field induced magnetostructural first-order transitions PM–FM at room temperature. These transitions might be accompanied by a large magnetocaloric effect. Low-temperature state in $Mn_{0.89}Cr_{0.11}NiGe$ exhibits antiferromagnetic properties and is extremely unstable relatively to the influence of even a small magnetic field. In general, $Mn_{0.89}Cr_{0.11}NiGe$ can be classified as promising materials for use in the application magnetocaloric at room temperatures in comparison with $MnNi_{0.9}Fe_{0.1}Ge$ (Fig. 5).

The first order magnetostructural phase transition from ferromagnetic to paramagnetic state is not realized in $MnNi_{0.90}Fe_{0.10}Ge$ with both types of heat treatment, that eliminates the appearance of sharp magnetic field induced transitions PM–FM. However, the FM state in quenched-on-wheel $MnNi_{0.90}Fe_{0.10}Ge$ is preserved to the lowest temperatures in distinct to $Mn_{0.89}Cr_{0.11}NiGe$. Based on set of magnetic properties, we can conclude that the iron contained samples are less promising for practical use.

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