



# *Article* **New Metastable Baro- and Deformation-Induced Phases in Ferromagnetic Shape Memory Ni2MnGa-Based Alloys**

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**Abstract:** Structural and phase transformations in the microstructure and new metastable baro- and deformation-induced phases of the Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub> alloy, typical of the unique class of ferromagnetic shape memory Heusler alloys, have been systematically studied for the first time. Phase X-ray diffraction analysis, transmission and scanning electron microscopy, and temperature measurements of electrical resistivity and magnetic characteristics in strong magnetic fields were used. It was found that in the course of increasing the pressure from 3 to 12 GPa, the metastable long-period structure of martensite modulated according to the 10*M*-type experienced transformation into a final non-modulated 2*M* structure. It is proved that severe shear deformation by high pressure torsion (HPT) entails grainsize refinement to a nanocrystalline and partially amorphized state in the polycrystalline structure of the martensitic alloy. In this case, an HPT shear of five revolutions under pressure of 3 GPa provided total atomic disordering and a stepwise structural-phase transformation (SPT) according to the scheme  $10M \rightarrow 2M \rightarrow B2 + A2$ , whereas under pressure of 5 GPa the SPT took place according to the scheme  $10M \rightarrow 2M \rightarrow B2 \rightarrow A1$ . It is shown that low-temperature annealing at a temperature of 573 K caused the amorphous phase to undergo devitrification, and annealing at 623–773 K entailed recrystallization with the restoration of the *L*2<sup>1</sup> superstructure in the final ultrafine-grained state. The size effect of suppression of the martensitic transformation in an austenitic alloy with a critical grain size of less than 100 nm at cooling to 120 K was determined. It was established that after annealing at 773 K, a narrow-hysteresis thermoelastic martensitic transformation was restored in a plastic ultrafine-grained alloy with the formation of 10*M* and 14*M* martensite at temperatures close to those characteristic of the cast prototype of the alloy.

**Keywords:** Heusler alloy  $Ni_{50}Mn_{28}$   $_{5}Ga_{21.5}$ ; martensitic transformations; megaplastic (severe) deformation; atomic disordering; nanostructure; properties

## **1. Introduction**

Alloys undergoing thermoelastic martensitic phase transformations (TMPTs) have a great innovative potential for a variety of structural and functional applications due to the effects of shape memory (SM), giant superelasticity (GS), elastic- and magnetocaloric (EMC) and other phenomena  $[1-10]$  $[1-10]$ . Notable among these alloys, of course, are the atomically ordered *L*2<sup>1</sup> Heusler alloys, which exhibit a ferromagnetic ordering below the Curie temperature  $T_C$  [\[10](#page-9-1)[–19\]](#page-9-2). For alloy compositions with the electron concentration *e*/*a* < 7.7, TMPT occurs from a ferromagnetic parent phase (i.e., *M<sup>s</sup>* < *TC*, where *M<sup>s</sup>* is the temperature at the start of martensitic transformation). A unique specific feature of Heusler ferromagnetic alloys based on the Ni-Mn-Ga system is the ability to control the TMPT, SM, GS, and EMC effects not only by temperature and external mechanical forces, as in other alloys [\[1–](#page-9-0)[9\]](#page-9-3), but also by the magnetic field [\[5,](#page-9-4)[10–](#page-9-1)[15\]](#page-9-5). During cooling below *Ms* , these alloys exhibit a sequence of first-order phase transitions from the parent cubic  $L2<sub>1</sub>$  phase to longperiod modulated intermediate martensite structures (denoted as 10*M* and 14*M*), as well



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as to tetragonal 2*M* martensite without lattice modulation [\[5\]](#page-9-4). A significant key limitation for wide practical application is the brittleness and poor machinability of ferromagnetic and other polycrystalline SM alloys, with the exception of titanium nickelide [\[1](#page-9-0)[–4,](#page-9-6)[16](#page-9-7)[,18](#page-9-8)[,20\]](#page-9-9). The high brittleness of  $Ni<sub>2</sub>MnGa-based$  alloys even in a single-crystalline state represents an obvious obstacle for realization of SM, GS, and other related effects.

There exist several ways to improve the ductility of intermetallics, among which grain size reduction and atomic disordering should be mentioned [\[5,](#page-9-4)[18\]](#page-9-8). It has been established that the combined technologies of ultra-rapid quenching (URQ) from the melt [\[21–](#page-9-10)[30\]](#page-10-0) and severe plastic deformation (SPD) [\[31](#page-10-1)[–36\]](#page-10-2) can provide production of SM alloys of individual chemical compositions based on titanium nickelide and copper, in a high-strength and ductile fine-grained (FG) [or ultra-fine-grained (UFG)] state. A URQ from the melt entails an increase in the strength and ductility of FG alloys with a mean grain size in the interval 0.2–1.0 µm, depending on the regime of subsequent thermal treatment. SPD provides for the formation of nanocrystalline UFG structure of the alloys (with the size of nanograins less than 100 nm). This leads to their strong hardening, but entails a decrease in their ductility. However, the ductility of these SPD UFG alloys can be significantly improved by subsequent low-temperature short-term annealing. An understanding of the combined treatment under discussion has been successful in (for example) the creation of wire demonstrating high strength and good plasticity, and of rods or sheets with SME for alloys based on titanium nickelide and copper. Recently, work on the creation of UFG structures using these methods of extreme external influences was performed on Ni<sub>2</sub>MnGa Heusler alloys by URQ from the melt [\[37–](#page-10-3)[43\]](#page-10-4), magnetron sputtering techniques [\[44](#page-10-5)[,45\]](#page-10-6) or the SPD methods [\[24,](#page-9-11)[46–](#page-10-7)[49\]](#page-10-8), including ball milling [\[50\]](#page-10-9).

In the present article, a comprehensive systematic analysis of structural-phase transformations was carried out for the first time in the three-component SM  $Ni<sub>2</sub>MnGa-based$ alloy, subjected to combined SPD by high-pressure compression (HPC) and subsequent high-pressure torsion (HPT), as well as heat treatment. This work studies the influence of applied HPC and HPT on the transformation behavior and evolution of physical electrical and magnetic properties in the investigated low elastic-modulus  $Ni_{50}Mn_{28.5}Ga_{21.5}$  alloy.

#### **2. Materials and Methods**

The Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub> alloy was melted out from nickel, manganese, and gallium of 99.99% purity in an electric arc furnace (Institute of Metal Physics, Ekaterinburg, Russia) in a helium atmosphere with triple remelting and subsequent long-term homogenizing annealing in the temperature range of 1073–1173 K. The chemical composition of the alloy according to integral spectral analysis was Ni–28.50 at.% Mn–21.50 at.% Ga. The grain sizes of the cast alloy reached several millimeters.

Samples for deformation in Bridgman anvils were made in the form of disks with a diameter (*D*) of up to 10 mm and a thickness (*t*) of 0.5 mm. The amplitude of high pressure was determined by the ratio of the value of applied load and the square of the anvil. True logarithmic deformation was determined as  $e = ln(t_i/t_f) + ln(\pi n D/t_f)$ , where  $t_i$  and  $t_f$  are the initial and the final thickness (of the sample), *n* is the number of revolutions. HPC deformation was performed at 3 and 12 GPa, and HPT deformation was performed at 3 GPa and five revolutions, and at 5 GPa and two and five revolutions HPC and HPT were carried out at room temperature (RT). The subsequent isothermal vacuum-sustained annealing was carried out for 10 min at temperatures in the interval of 373–973 K.

The phase composition and structural-phase transformations were studied by X-ray diffraction (XRD, Empyrean "PANalytical", in monochromatized CuKα radiation) (Malvern Panalytical B.V, Almelo, The Netherlands), analytical scanning (SEM, Quanta 200 Pegasus at 30 kV) (FEI Europe B.v., Eindhoven, The Netherlands) and transmission electron (high-resolution TEM, Tecnai  $G^2$  30 and CM30 at 300 kV) (FEI Europe B.v., Eindhoven, The Netherlands) microscopy, including in situ investigations under heating or cooling.

The temperature measurements of electrical resistivity and magnetic characteristics were carried out by the potentiometric method, on the MPMS-5XL SQUID magnetometer (Quantum Design, San Diego, CA, USA) and on the PPMS-9 installation (Quantum Design, San Diego, CA, USA), and the temperatures at the start ( $M_s$ ,  $A_s$ ) and finish ( $M_f$ ,  $A_f$ ) of the forward  $(M_s, M_f)$  and reverse  $(A_s, A_f)$  TMPTs of the alloy were determined using the two tangent method.

# **3. Results and Discussion**

According to the XRD analysis data, the initial cast coarse-grained alloy Ni<sub>50</sub>Mn<sub>285</sub>Ga<sub>21.5</sub> after synthesis was in a state of modulated long-period 10*M* martensite (Figure [1a](#page-2-0), Table [1\)](#page-2-1) [\[51](#page-10-10)[,52\]](#page-11-0).

<span id="page-2-0"></span>

3 GPa, (c) at 12 GPa; after HPT at 5 GPa at (d) 2 and at  $(e,f)$  five revolutions. The observations were performed at  $(a-e)$  RT and  $(f)$  130 K. **Figure 1.** X-ray diffractograms of Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub> alloy (a) in the initial cast state; (**b**) after HPC at

<span id="page-2-1"></span>**Table 1.** Type, crystal structure parameters  $(a, b, c)$ , and specific atomic volume  $(V)$  of phases in the  $\frac{1}{2}$  s<sub>how</sub> the  $\frac{1}{2}$ <sub>0.9</sub> s  $\frac{1}{2}$ <sub>1.0</sub> alloy  $Ni_{50}Mn_{28.5}Ga_{21.5.}$ 

<b>Type of Structure</b>	<b>Space Group</b>	a, nm	$b. \, \text{nm}$	$c$ , nm	$V.$ nm <sup>3</sup>
10 <i>M</i> /orthoromb.	Pnnm	0.422	0.558	2.098	0.01235072
2M/tetragon.	14/mmm	0.5512		0.6562	0.01246048
B2/BCC	Pm3m	0.2923			0.01248695
$\gamma$ -A1/FCC	Fm3m	0.3684			0.01249968

<span id="page-3-0"></span>Figure 2 shows the hierarchy [of](#page-3-0) the packet micromorphology of 10M martensite in the cast alloy. It is seen that the packet micromorphology is formed by primary microcrystals (Figure [2a](#page-3-0)), twinned pairwise according to the data from electron back-scattered diffraction (EBSD) (Figure 2c,d), and contains larger magnetic microdomains in accordance with Lorentz microscopy (Figure 2b).



Figure 2. SEM images of (a) the packet microstructure of 10M martensite in the initial cast alloy Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub> in secondary electrons; (b) magnetic domains under Lorentz microscopy, and microcrystals with a thickness of ~1 micron of twin orientation according to EBSD. (**c**,**d**) microcrystals with a thickness of ~1 micron of twin orientation according to EBSD. **igure 2.** SEM images of (**a**) the packet microstructure of 10M martensite in the initial cast alloy

Figure 3 shows that, according to TEM data, secondary nanotwins were present inside individual martensite crystals. Figure [3a](#page-3-1) demonstrates the mechanism of intragrain formation of a packet of nano-twinned 10M martensite crystals in a TEM in situ experiment after heating by an electron beam. In the regions of the residual initial high-temperature  $L2_1$ phase, a typical pre-martensitic tweed contrast is visible, accompanied by the appearance of diffuse streaks along <110> and satellites in positions of type  $1/6$  <220>  $L2_1$  in the SAED patterns (see Figure [3a](#page-3-1)). Cooling in situ TEM from RT to 120 K led to the second TMPT with the formation of nano-twinned long-period 14*M* martensite packets (Figure [3b](#page-3-1)) [\[52](#page-11-0)[–54\]](#page-11-1).

<span id="page-3-1"></span>

**Figure 3.** Bright-field TEM images of the microstructure of the cast alloy Ni50Mn28.5Ga21.5 at (**a**) RT and (**b**) 120 K and the corresponding micro electron diffraction patterns (SAED, in the inserts). The SAED patterns correspond to residual *L*21 austenite (zone axes (a.z.) [010] *L*21, insert on the left in thin nanotwins of the  $10M$  (a.z. [010]  $10M$ , insert on the right in (a) and the  $14M$  (a.z. [111] former  $L2<sub>1</sub>$ , insert in (b) martensite. The observations were performed at (a) RT and (b) 120 K. Figure 3. Bright-field TEM images of the microstructure of the cast alloy  $\text{Ni}_{50}\text{Mn}_{28.5}\text{Ga}_{21.5}$  at (a) RT and (**b**) 120 K and the corresponding micro electron diffraction patterns (SAED, in the inserts). The and (**b**) 120 K and the corresponding micro electron diffraction patterns (SAED, in the inserts). The SAED patterns corresponding material *L21* austenite (*z*one and *L21 austenberg (and L21 august 10 au* SAED patterns correspond to residual  $L2_1$  austenite (zone axes (a.z.) [010]  $L2_1$ , insert on the left in (a),

According to the XRD data, HPC at 3 and 12 GPa affected the phase composition of the alloy (Figure [1b](#page-2-0),c), leading to partial (after 3 GPa) or complete TMPT (after 12 GPa) into the so-called non-modulated martensite with tetragonal structure of type 2*M* (Table [1\)](#page-2-1). The grain sizes, as a rule, did not change, despite the tenfold excess of pressure at HPC over the strength limit of this low-modulus alloy. An application of HPT under a pressure of 5 GPa and two and five revolutions caused further radical phase changes with formation in the alloy—according to th[e](#page-2-0) XRD analysis—of the γ-FCC structure (of type *A*1) (see Figure 1d-f; and Table 1). At the same time, after HPT for two revolutions, the preservation of traces of the *L*2<sub>1</sub> phase [w](#page-2-0)as note[d \(](#page-2-1)Figure 1d*,* Table 1).

the allow (Figure 1b,c), leading to partial (after 3 GPa) or complete TMPT (after  $3$ 

According to the TEM data, HPT under a pressure of 3 GPa and five revolutions According to the TEM data, HPT under a pressure of 3 GPa and five revolutions completely changed the microstructure of the alloy (Figure 4a). The dark-field TEM image completely changed the microstructure of the alloy (Figur[e 4](#page-4-0)a). The dark-field TEM image of the alloy structure shows that the sizes of nano crystallites were 10–20 nm. When cooled of the alloy structure shows that the sizes of nano crystallites were 10–20 nm. When cooled to 120 K in the mode of TEM in situ, the dimensional and morphological features of the to 120 K in the mode of TEM in situ, the dimensional and morphological features of the nanostructured *B*2 state in the alloy were preserved (insert in Figure 4a). The reflections nanostructured *B*2 state in the alloy were preserved (insert in Figur[e 4](#page-4-0)a). The reflections in the SAED pattern (see the insert in Figure 4[a\)](#page-4-0) were distributed over the rings and had the following *hkl B*2-phase indices: 100, 110, 200, 211, etc. Moreover, judging by the halo—a weaker individual diffusive ring near the 100 position—the alloy was in a partially amorphous state at cooling up to 120 K. Methodically reliable identification of the β phases amorphous state at cooling up to 120 K. Methodically reliable identification of the β phases *L*21, *B*2, and *A*2 was provided only by visualization of weak superstructural reflections *L*21, *B*2, and *A*2 was provided only by visualization of weak superstructural reflections in in the SAED patterns of the types 111 and 200 from *L*2<sub>1</sub>, 100 from *B*2, or their absence for the *A*2 structure. In this case, we can only conclude unequivocally that the  $(B2 + A2)$ nanostructure is dominant in the alloy, since super-structure reflection of 111 *L*2<sub>1</sub> type was absent in the SAED patterns. absent in the SAED patterns.

<span id="page-4-0"></span>

Figure 4. (a,c) Dark- and (b) bright-field TEM images of the nanostructure, and (d) a direct resolution  $t_{\text{max}}$  is the atomic structure of the  $N_{\text{max}}$ .  $\sigma$  allows  $\frac{1}{\sigma}$ . The  $t_{\text{max}}$  and  $\frac{1}{\sigma}$  is  $\frac{1}{\sigma}$ . image of the atomic structure of the  $Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub>$  alloy subjected to HPT at five revolutions at (a) 3 GPa and (b–d) 5 GPa, and corresponding SAED patterns (in the inserts). The observations were performed (**a**,**b**,**d**) at RT and (**c**), insert in (**a**) at 120 K.

After HPT at a pressure of 5 GPa and five revolutions, similar TEM images of the After HPT at a pressure of 5 GPa and five revolutions, similar TEM images of the nanostructured state of the alloy were observed. However, SAED patterns had fundamen-nanostructured state of the alloy were observed. However, SAED patterns had funda-manostructured state of the alloy were observed. The wever, of the patterns had randa-<br>mentally changed (inserts in Figure [4b](#page-4-0),c). According to the results of their indexing, in accordance with the XRD analysis (Figure [1e](#page-2-0),f) the alloy has a structure of  $γ$ -FCC up to accordance with the viris dridly one (1 gare 1 c), the alloy has a structure of  $\gamma$  1 ce ap to 120 K (of type *A*1: with *hkl* indices 111, 200, 220, 311, etc.). It can be assumed that the amorphous component detected due to continuous diffuse halos (inserts in Figure [4a](#page-4-0)–c) on the blurred, sinuous intercrystalline interfaces of γ nanocrystals clearly visualized in was localized on the blurred, sinuous intercrystalline interfaces of γ nanocrystals clearly visualized in direct atomic resolution images (Figure [4d](#page-4-0)). It is along these that the bending visualized in direct atomic resolution images (Figure 4d). It is along these that the bending contours of extinction were localized in TEM images.

As was already noted, XRD analysis showed that the  $Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub>$  alloy subjected to HPT at 5 GPa and five revolutions, in accordance with TEM data, had a γ-FCC structure of type *A*1 (Figure [1e](#page-2-0),f), which was preserved during cooling in situ to 130 K. However, all the Bragg reflections were noticeably broadened. Annealing at 373 and 473 K did not change the described nanostructural  $\gamma$  state of the HPT-ed alloy (Figure [5a](#page-5-0),b). After annealing at 573 K,



<span id="page-5-0"></span>the diffuse halo on the SAED patterns had almost disappeared, indicating the realization of a thermally activated process of devitrification of the amorp[ho](#page-5-0)us component (Figure 5c). nealing at 573 K, the diffuse halo on the SAED patterns had almost disappeared, indicatthe diffuse halo on the SAED patterns had almost disappeared, indicating the realization of

Figure 5. (a-c) Dark-field TEM images of the microstructure and corresponding SAED patterns  $t_{\text{S}}$  and  $t_{\text{S}}$ . The Nissan mages of the introduction that  $\epsilon$  and  $\epsilon$  and  $\epsilon$  revolutions and subset-(in the inserts) of the  $\text{Ni}_{50}\text{Mn}_{28.5}\text{Ga}_{21.5}$  alloy subjected to HPT at 5 GPa and five revolutions and subsequent annealing at (**a**) 373 K, (**b**) 473 K, (**c**) 573 K for 10 min. TEM observations were performed at RT (**a**–**c**), SAED at (**a**—left SAED) RT and (**a**–**c**—right SAED) 120 K. RT (**a**–**c**), SAED at (**a**—left SAED) RT and (**a**–**c**—right SAED) 120 K.

<span id="page-5-1"></span>Annealing at 623 K led to more noticeable structural changes in the allow (Figure 6). Annealing at 623 K led to more noticeable structural changes in the alloy (Figure [6\)](#page-5-1). As a create of the primary correspondence of 50–150 nm. However, in the insert in the insert in the insert in the i in the wide range of 50–150 nm. However, in the SAED pattern of the insert in Figure [6b](#page-5-1),<br>concentrational reflections distributed by the since (of trans 100 form the  $P2$  ca 111 cm 1200 from the  $L_2$ <sub>1</sub> phases) were not practically resolved, excluding individual marked reflections (200 L<sub>21</sub>, 125 10M, 127 14M). Cooling to 120 K revealed the presence of 10M martensite reflections (for example, see Figure [6d](#page-5-1), insert). Figure [6c](#page-5-1),d shows bright- and dark-field TEM images of twinning inside martensitic grains larger than 100 nm. It can be assumed can be assumed that TMPT occurred in *L*21 grains. that TMPT occurred in *L*2<sup>1</sup> grains. can be assumed that TMPT occurred in *L*21 grains. a result of the primary recrystallization, the size of the nanograins significantly increased superstructural reflections distributed by the rings (of types 100 from the *B*2, or 111 and 200



**Figure 6.** (**a**,**c**) Bright- and (**b**,**d**) dark-field TEM images of the microstructure and corresponding SAED patterns (in the inserts) of the  $Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub>$  alloy subjected to HPT at 5 GPa and five revolutions and subsequent annealing at 623 K for 10 min. Observations were performed at (**a**,**b**) RT and (**c**,**d**) 120 K.

<span id="page-6-0"></span>Recrystallization annealing at 773 K caused more noticeable grain growth and, obvi-Recrystallization annealing at 773 K caused more noticeable grain growth and, obviously, a complete restoration of the perfect metastable *L*2<sup>1</sup> superstructure. The grain sizes ously, a complete restoration of the perfect metastable *L*21 superstructure. The grain sizes did not exceed 400 nm. As a result, 10*M* martensite in the UFG state was observed at RT did not exceed 400 nm. As a result, 10*M* martensite in the UFG state was observed at RT (Figure 7a,b). When cooled by the in situ TEM method, the alloy experienced a second (Figure [7a](#page-6-0),b). When cooled by the in situ TEM method, the alloy experienced a second TMPT of the 10*M* → 14*M* type (Figure 7c,d). After annealing at 873 K, the grain sizes did TMPT of the 10*M* → 14*M* type (Figure [7](#page-6-0)c,d). After annealing at 873 K, the grain sizes did not exceed 1 micron. The nanotwin morphology of 14*M* martensite inherited from 10*M* not exceed 1 micron. The nanotwin morphology of 14*M* martensite inherited from 10*M* martensite also differed, as in the case of 10*M*, by the exceptionally single-packet character martensite also differed, as in the case of 10*M*, by the exceptionally single-packet character of individual grains. of individual grains.



Figure 7. (a,c) Bright- and (b,d) dark-field TEM images of the microstructure and corresponding  $\sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n}$ SAED patterns (in the inserts) of the Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub> alloy subjected to HPT at 5 GPa and five revolutions and subsequent annealing at 773 K for 10 min. Observations were performed at  $(a,b)$  RT and (**c**,**d**) 120 K.

 $T$  in the NiSO  $\alpha$  allow, it is established that as the pressure value and the pr Thus, in the  $Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub>$  alloy, it is established that as the pressure value and deformation-induced that as the pressure value and stepwise structural-phase transformation occured according to the scheme 10*M* → 2*M* → the degree of shear SPD increased, a baro- (pressure-provided) and deformation-induced stepwise structural-phase transformation occured according to the scheme  $10M \rightarrow 2M$  $\rightarrow$  *B*2 $\rightarrow$  *A*1, and at the same time cascade-wise atomic disordering occured. The effect of other in the same time debates *B*2-*BCC*, *A*1-*FCC*, and *L*2, sustant to with or submisation of the nanostractured phases *b*2 *b*CC, *i*<sup>1</sup> **i** CC, and *E*<sub>I</sub><sup></sup> dustently what respect to TMPT was found at a critical grain size of up to 100 nm when the alloy was respect to 11.1 T was found at a critical grain size of up to 100 km when the anof was cooled to 120 K. The obvious reasons for the suppression of TMPT in Ni-Mn-Ga-based EU ALLO IN THE CULTURE FULL AS IN THE CULTURE OF THE CONDUCT OF THE PART IN THE CHILD CONDUCT.<br>Heusler alloys and the like, as well as in titanium nickelide alloys, are (i) deformationreduction in the size of nanograins below the critical level, (ii) atomic disordering, (iii) induced reduction in the size of nanograins below the critical level, (ii) atomic disordering,  $\alpha$  mattee related in the size of nanograms serve are entited every (ii) amorphization, and (iv) the detected sequential SPT  $10M \rightarrow 2M \rightarrow B2 \rightarrow A1$ . The subsequent recrystallization annealing ensures (i) the growth of grains characteristic of the UFG state, (ii) restoration of the atomic order inherent to the *L*2<sub>1</sub> type, and, as a result, (iii) restoration of reversible TMPTs. of stabilization of the nanostructured phases *B*2-BCC, *A*1-FCC, and *L*2<sup>1</sup> austenite with

The baro-induced transition  $10M \rightarrow 2M$  occurred (i) under the influence of high pressure at 3 and 12 GPa with an increase in the value of the specific volume, as well as (ii) in the nanophases *B*2 and *A*1 formed in the course of HPT at high pressure of 3 and 5 GPa (at  $n = 2$  or 5, respectively, see Table [1\)](#page-2-1). Consequently, the appearance of the observed phases in the sequence  $10M \rightarrow 2M \rightarrow B2 \rightarrow A1$  was due not so much to the pressure as to the actual intense SPD (for example, *e* = 7 after five revolutions at the site of .<br>half of the disk radius). Both pressure-induced (under the influence of high pressure) and deformation-induced (under shear SPD) phase transitions were accompanied by atomic and structural disordering. It is this phenomenon that actually determined the key physical nature of the detected phase transitions. It is obvious that in this case, annealing, which restored the atomic order and type of superstructure, as well as grain size above the critical level with a significant decrease in the number and density of defects in their internal

structure, led to the implementation of reversible TMPTs inherent in the alloy, as found in the investigations conducted.

show the directions of the temperature change cycles during measurements of *ρ*(*T*), start-

A more complete physical interpretation of data obtained for the first time on new deformation-induced phases and structural-phase transformations in the Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub> alloy was provided by using the results of temperature measurements of electrical resistivity  $\rho(T)$  in the initial ca[st](#page-7-0) state and after HPT (Figure 8a,b). In the figure, the arrows show the directions of the temperature change cycles during measurements of  $\rho(T)$ , starting from RT to 4.2 K during cooling, then up to 800 K during heating, reverse cooling to 4.2 K and again reheating to RT. First, it can be seen that the dependence  $\rho(T)$  changed after the HPT. Namely, the alloy subjected to HPT had high values of  $ρ = 140 μΩ$ ·cm below 400 K, and its low-temperature behavior was characterized by an anomalous negative temperature coefficient of resistivity (TCR) compared to the normal TCR for the original cast prototype alloy. The value of the residual electrical resistivity  $\rho_0$  at a temperature of 4.2 K in the studied HPT samples showed an almost four-fold increase compared to the value  $\rho_0$  of the cast alloy.

<span id="page-7-0"></span>

Figure 8. (a,b) Temperature dependences of electrical resistivity  $\rho(T)$  and (c) magnetization  $M(T)$  of  $N_{150}M_{128,5}G_{21.5}$  alloy in the initial cast state or (c) after HPT at five revolutions and 5 GPa (curves 1 at 0.8 MA/m, 2 and 3 at 4 MA/m). *Curve* 3, right ordinate axis. at 0.8 MA/m, 2 and 3 at 4 MA/m). *Curve* 3, right ordinate axis.

Second, in the high-resistivity HPT alloy, the characteristic anomalies inherent to the TMPTs were not observed on the curves  $\rho(T)$ . Finally, subsequent heating in the interval from 600 to 800 K led to a decrease in  $\rho(T)$  almost to the value of the initial cast alloy, and then the appearance of a narrow hysteresis loop due to the reversible TMPT (Figure [8b](#page-7-0)). The measured critical temperatures of TMPTs are given in Table [2.](#page-7-1) The behavior of  $\rho(T)$ during heating after cooling, shown in Figure [8b](#page-7-0), clearly reveals two stages: relaxation of elastic-plastic distortions (recovery) in the temperature range from RT to 550 K and recrystallization in the range 550–800 K.

<span id="page-7-1"></span>Table 2. Critical temperatures of the TMP-transformed alloy Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub>.

Condition	$M_{\rm s}$ , K	$M_f$ , K	$A_{s}$ , K	$A_f$ , K	ΔΜ	ΔΑ	ΔΤ	$T_C$ , K
Cast alloy/ $\rho(T)$ , Figure 8a	311	304	311	315				395
Cast alloy/M(T), Figure 8c, curve 1	311	302	312	322		10	10	395
Cast alloy/M(T), Figure 8c, curve 2	319	309			10			395
HPT at 5 GPa at 5 revolutions/ $\rho(T)$ , Figure 8b	287	276	282	293				400

Figure [8c](#page-7-0) shows the results of measurements of the magnetic properties of the  $Ni<sub>50</sub>M<sub>28.5</sub>Ga<sub>21.5</sub>$  alloy in the cast state and after HPT. When analyzing the magnetization of *M*(*T*), measurements were carried out starting from RT down to 4.2 K when cooling, then when heating to 400 K (*curves* 1 and 2) or up to RT (*curve* 3). From the data obtained, it can be seen that the application of a strong magnetic field  $H = 4$  MA/m increased the temperatures of  $M_s$  and  $M_f$  by 10 and 5 K, respectively (Table [2\)](#page-7-1). Also, attention is drawn to the sharp decrease in the magnetization of *M(T)* at RT in the HPT alloy compared to

*M(T)* of the prototype alloy. However, when cooled to 4.2 K, the value of *M(T)* increased noticeably (Figure [8c](#page-7-0), *curve* 3). The magnetization *M(T)* on cooling approached the value 60 A $\cdot$ m<sup>2</sup>/kg, whereas for the alloy in the initial state the value of its magnetization  $M(T)$ was greater than 80 A·m<sup>2</sup>/kg. Thus, analysis of the results of the structural studies and physical measurements shows that when the temperature drops below RT, despite the lower magnetization value, the HPT-ed  $\gamma$  alloy is in a partially magnetically ordered state, obviously genetically related to the original *L*2<sup>1</sup> alloy structure.

In conclusion, we note that the HPT-ed alloy, like its prototype alloy, experienced brittle fracture–destruction when bending. At the same time, after the formation of the UFG structure during annealing at 773 K and 873 K, the alloy became sufficiently plastic to bend and under subsequent heating experienced reversible deformation into a flat shape, showing SM effect.

### **4. Summary and Conclusions**

In this work, we established the effect of SPD on  $Ni<sub>50</sub>Mn<sub>28.5</sub>Ga<sub>21.5</sub>$  alloy using highpressure uniaxial compression (HPC) and torsion (HPT). The following main conclusions are made:

- 1. It was found that with an increase in pressure from 3 to 12 GPa, a metastable longperiod 10*M* martensitic structure underwent a baro-induced transformation into a non-modulated 2*M* structure.
- 2. HPT radically refined the polycrystalline grain structure to a nanocrystalline, partially amorphized state at the grain junctions. As the pressure increased (up to 5 GPa) and the degree of deformation achieved the value of true deformation  $e = 7$  (after five revolutions), a deformation-induced atomic disordering evolved and a stepwise structural-phase transformation occurred according to the scheme 10*M*→2*M* → *B*2→*A*1.
- 3. HPT shear of five revolutions under a pressure of 3 GPa provided incomplete deformationinduced atomic disordering and a stepwise structural-phase transformation according to the scheme  $10M \rightarrow 2M \rightarrow B2 + A2$ .
- 4. Annealing at a temperature of 573 K caused the amorphous phase to decompose, and recrystallization annealing at 773–873 K entailed the formation of the *L*2<sup>1</sup> UFG structure characterized by a narrow-hysteresis TMPT with critical temperatures close to those characteristic of the cast prototype alloy.
- 5. It was found that the dimensional effect of complete stabilization of a nanostructured alloy with respect to TMPT when cooled to 120 K was realized at a grain size of less than 100 nm.
- 6. The electrical resistivity of the HPT-ed  $\gamma$  alloy increased significantly during cooling, demonstrating a negative value of temperature coefficient of resistivity. In this case, the alloy was in a partially magnetically ordered high-resistivity state, the magnetization of which increased significantly in strong magnetic fields at low temperatures.
- 7. It can be assumed that the creation of a UFG structure in the alloy allowed its ductile properties to increase to those necessary for the implementation of an SM effect.

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