Journal of Applied Physics

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Cite as: J. Appl. Phys. **127**, 175103 (2020); https://doi.org/10.1063/5.0003287
Submitted: 31 January 2020 . Accepted: 05 April 2020 . Published Online: 04 May 2020

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Journal of Applied Physics ARTICLE scitation.org/journal/jap

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Published Online: 4 May 2020

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Note: This paper is part of the Special Topic on: Multicalorics.
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ABSTRACT

The results of *in situ* studies of the magnetostructural transition occurring in single crystals of an $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy are presented in this paper. The formation of martensitic twins on exposure to high magnetic fields up to 10 T in the magnetostructural transition regime was observed using an indigenously developed optical microscope. Experiments on magnetization were performed on single crystals of $Ni_{2.19}Mn_{0.81}Ga$ in high magnetic fields, a phase diagram between magnetic field and temperature was constructed, and the isothermal entropy change was estimated. Based on the experimental data and the results from optical microscopic examination, the influence of magnetic field and thermal cycling on martensitic twins and, in turn, on the magnetocaloric effect, is discussed.

I. INTRODUCTION

In recent years, a large number of research papers have been devoted to the study of the magnetocaloric effect (MCE). MCE is an adiabatic temperature change (ΔT_{ad}) that a magnetic material undergoes in the presence of a magnetic field. MCE is studied for a wide range of materials [e.g., compounds that are based on MnAs, $Gd_5(SiGe)_4$, Ni–Mn–X (X = Ga, In, Sn, and Sb) (Heusler alloys), La (Fe, Si)$_{13}H_x$, MnTMX (TM = Co, Ni, and Fe; X = Si and Ge), etc.],[1,2] either by direct[3–10] or indirect methods,[8–12] in the presence of weak[13–18] or high magnetic fields.[19–29] It is well known that the peak in MCE is observed near regions, where magnetic phase transitions occur. The magnetostructural phase transitions exhibited by some Heusler alloys have captivated the interest of researchers. In the magnetostructural phase transition region, MCE has two major contributions.[10,11] These contributions emerge from the magnetic and structural subsystems that can have both positive and negative contributions to MCE, and, accordingly, they compete with each other depending on the number of cycles the sample is subjected to in a magnetic field.[13,18,30,31] One of the first reports on the influence of cycling of the Heusler alloy sample in a magnetic field was published by Khovaylo *et al.*[30] This work pertained to single crystals of $Ni_{2.19}Mn_{0.81}Ga$ alloy and showed a decreasing adiabatic temperature change (ΔT_{ad}) with increasing number of cycles (N) in a magnetic field ($\mu_0 H$) of magnitude 1.85 T. For example, for $N = 1$, the adiabatic temperature change (ΔT_{ad}) is 1.2 K, while that for $N = 6$ is 0.6 K.[30] Also, interesting results on MCE were obtained[18] for the $Ni_{47}Mn_{40}Sn_{12.5}Cu_{0.5}$ alloy sample discussing the influence of frequency of cycling in a magnetic field. At the temperature of testing ($T = 277$ K), on the first turn-on of the magnetic field, the $Ni_{47}Mn_{40}Sn_{12.5}Cu_{0.5}$ alloy shows an inverse MCE and $\Delta T_{ad} = -1$ K at $\mu_0 H = 1.8$ T. For each subsequent cycling of the sample in a magnetic field, the magnitude of MCE decreases, and on the sixth

cycle, the alloy shows direct MCE and $\Delta T_{ad} > 0$, for $\mu_0 H = 1.8$ T and $T = 277$ K. In the examples cited,[13,18] it is assumed that the MCE sharply depends on cycling in a magnetic field due to the irreversibility of microstructural transformation under the influence of high magnetic fields.[32] In turn, the irreversibility of the microstructural transformation is associated with characteristic hysteresis arising from the first order phase transition. In Ref. 33, emphasis is laid on the fact that nucleation makes the major or prime contribution to the characteristic hysteresis of the first order phase transition. The subject of nucleation[13,34,35] and its effect on MCE for Heusler alloys[13,32,36] has rarely been discussed in the recent literature in the field.

The paper by Grechishkin *et al.*[34] is devoted to the study of motion of the phase boundaries during microstructural transition under the influence of temperature in an $Ni_{2.12}Mn_{0.88}Ga$ Heusler alloy. It can be observed that on passing across the sample, the initially corrugated austenite/martensite boundary leaves an uncorrugated surface behind. This process is reversible and occurs repeatedly. However, quite the opposite trend was observed by Gottschall *et al.*[13] In $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ Heusler alloy, after every thermal cycling, i.e., fully transformed austenite–martensite phase transition under the influence of temperature, the low-temperature martensite phase shows a completely different configuration. According to Gottschall *et al.*,[13] this is due to the fact that the martensite nuclei have some arbitrary character in terms of position and orientation. Depending on the nature of the position and orientation of the martensite nuclei, the low-temperature phase develops differently.[13] A fewer number of research papers have appeared in recent times on martensitic transformation and its effect on MCE is due to the availability of advanced characterization techniques, such as x-ray diffraction and neutron diffraction, for studying the crystal structure. However, difficulties are involved in applying these techniques for structural studies in high magnetic fields. Therefore, the authors of this article suggest studying the microstructural transition by a specially developed optical microscope in high magnetic fields.[37] Moreover, this work gives greater attention to the magnetic-field-induced martensitic phase nucleation in high magnetic fields for single crystals of the $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy and its effect on MCE studied earlier by Khovaylo *et al.*[30]

II. SAMPLE AND EXPERIMENTAL DETAILS

Single crystals of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy were prepared by the Czochralski method. The crystal growth direction was chosen parallel to the [110] direction in the inoculum crystal. To prepare single crystals of $Ni_{2.19}Mn_{0.81}Ga$ alloy, the elements were initially weighed and taken in appropriate quantities so as to adhere to the composition of $Ni_{2.3}Mn_{0.97}Ga$, and the crystals were grown at a temperature of 1110–1130 K.

The metallographic preparation of the samples for microstructural studies was carried out by machining.[34] An important aspect of the preparation of Heusler alloy samples is that the polishing should be carried out above the martensitic transition temperature, i.e., in the austenitic state of the alloy. As a result, features pertaining to martensite relief appear on the surface of the sample on cooling of the alloy below the magnetostructural transition.

Quantum Design's PPMS-9T physical property measuring system was used for the magnetization studies. The PPMS-9T system helps conduct experiments automatically in the temperature range of 1.8–400 K and in magnetic fields up to 9 T.

To study the magnetic-field-induced microstructural evolution in high magnetic fields, an indigenously developed optical microscope was used[37] in the present study. The optical microscope helps *in situ* observation of microstructural changes that are introduced due to the occurrence of first order phase transition on exposure to high magnetic fields generated by a Bitter coil magnet in a wide range of temperatures and varying thermodynamic conditions. The optical microscope is made of non-magnetic materials, and the main optical system consists of an objective-lens and a thermostat chamber. A vacuum level of 10^{-4} Torr is maintained in the working chamber using a vacuum pump. A polished sample is fastened to the surface of a massive working table using thermally conducting glue. The working table is made of non-magnetic brass and has a heating system. The working table with the sample is located in the thermostat chamber. The hot junction of a copper–constantan thermocouple is directly glued to the sample. This facilitates controlling and maintaining the set temperature of the sample during the turn-on/off of the magnetic field. The temperature changes of the sample, caused by the possible influence of the MCE, did not exceed 0.1 K. The sample was illuminated by LEDs. The images of the microstructure of the surface of the sample were recorded using a video camera located in the upper part of the microscope. The scanning rate of the magnetic field was about 14 T/min. More relevant details pertaining to these studies can be found in Ref. 37. It should be noted that microstructural studies using the optical microscope make it possible to estimate the characteristic temperatures of a magnetic-field-induced structural transition by observation. Each turn-on/off of the cycle of magnetic field introduces some features into the martensitic transition that are observed on the metallographically prepared surface of the sample. However, the magnetic-field-induced transition and the nucleation behavior of martensitic twins are reproduced regularly without critical changes. The size of martensitic twins upon nucleation is relatively large (refer to the scale in the micrographs). Therefore, this also increases the reproducibility of determining the characteristic temperatures of the magnetic-field-induced structural transition.

The microstructural observations attesting the occurrence of the martensitic transition in the single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy were done using the optical microscope[37] by following certain procedures. To explain the protocol, the following transformation temperatures of experiment are taken into account: M_s and M_f are the martensite start (nucleation) temperature and martensite finish (growth) temperature, respectively, while A_s and A_f are austenite start (nucleation) temperature and austenite finish (growth) temperature, respectively. T_{exp} is the initial temperature of the experiment, which is set to a constant value before magnetization/demagnetization of the sample. To start with, the required sample temperature (T_{exp}) is established. It is followed by the occurrence of sample magnetization/demagnetization. A magnetic field of sufficient magnitude induces a structural transition from austenite to martensite, and vice versa. An important parameter of the study is the initial temperature of the experiment (T_{exp}). The

larger the difference in temperature ($T_{exp} - M_s$), the greater the magnetic field that is required so as to induce as well as complete the magnetostructural transition. Three conditions of the experiments are adopted in the work. These are cooling/heating without/after thermal cycling. Cooling involves slow cooling of the sample to T_{exp} after being heated to above A_f. Heating involves gradual heating of the sample after having cooled it to below M_f. The phrase "after thermal cycling" refers to the condition when subsequent T_{exp} was followed by the additional step of heating to A_f. The phrase "without thermal cycling" refers to the condition when each subsequent T_{exp} was not accompanied by the additional step of heating to A_f.

III. RESULTS AND DISCUSSION

A single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy exhibiting direct MCE in the magnetostuctural phase region was chosen as the material[30] for the study. This alloy belongs to the family of $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys.[38,39] From the phase diagram of the $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys,[38] it is found that two phase transition regions merged into one in the specific case of the $Ni_{2.19}Mn_{0.81}Ga$ alloy. These two transitions involve a second order paramagnetic to ferromagnetic transition and a first order thermoelastic martensitic transformation from the high temperature austenitic phase (cubic) to the low temperature martensitic phase. To elaborate the phase transitions occurring at the characteristic transformation temperatures in the single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy and to demonstrate the behavior of thermal hysteresis in high magnetic fields, the variation of magnetization (M) in magnetic fields up to 7 T were determined [Fig. 1(a)] using a Quantum Design's PPMS-9T physical property measuring system. As can be seen from Fig. 1(a), the single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy undergoes a magnetostructural phase transition above room temperature.[40] The magnetization decreases sharply with increase in temperature, while at the same time, a microstructural transition occurs from martensite to austenite. On cooling, the magnetization increases sharply, and the microstructure changes from austenite to martensite.[38,40] An increase in the applied magnetic field causes a shift in the characteristic thermal hysteresis to the higher temperature region.[40] It should be noted that for the $Ni_{2.19}Mn_{0.81}Ga$ alloy, the saturation magnetization of martensite (low temperature phase) is higher than that of austenite (high temperature phase). Therefore, at a constant temperature, near the phase transition region in the austenitic phase, applying a sufficiently high magnetic field causes the nucleation of martensite that is accompanied by the formation as well as the growth of martensitic twins.[41]

Using the linear extrapolation method for the intersection of extrapolations of the magnetization temperature dependence for corresponding structural phase [Fig. 1(a)], the characteristic temperatures of the magnetostructural transitions were determined [Fig. 1(b)]. Their values are estimated by linear fitting at different magnetic fields (0.3, 1, 2, 5, and 7 T). The characteristic temperatures determined at 0 T magnetic field are $A_s = 320$ K, $A_f = 325$ K, $M_s = 318$ K, and $M_f = 313$ K. The error on determining the characteristic temperatures of the magnetostructural transition at 0 T was calculated as the standard deviation for a linear fitting of these values in a magnetic field. Thus, the error on determining all the

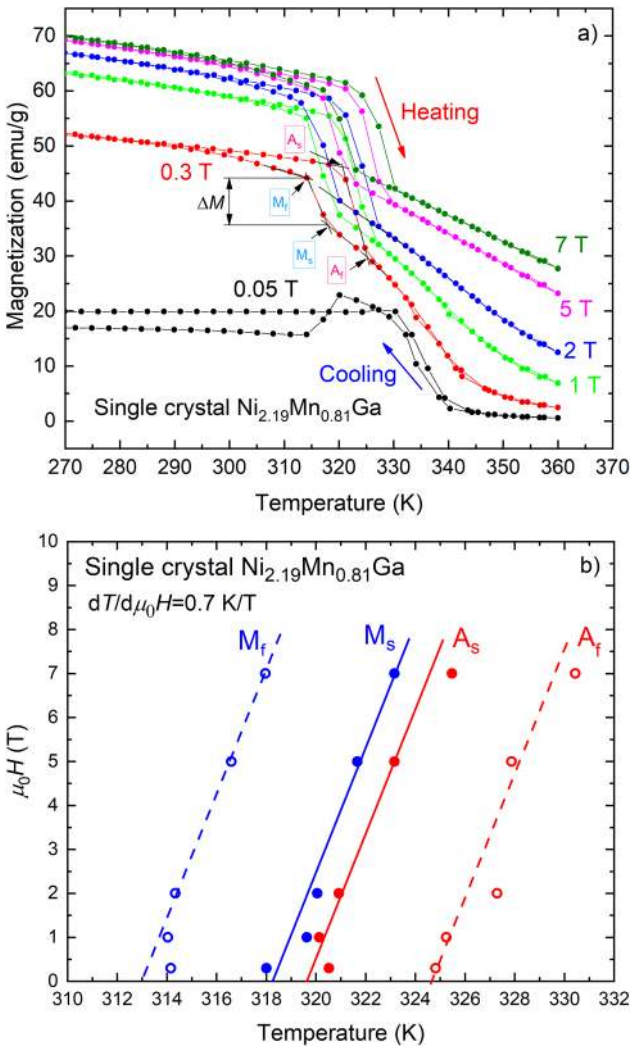

FIG. 1. (a) Temperature dependence of magnetization of a single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy in varying magnetic fields, i.e., $\mu_0 H = 0.05 \ldots 7$ T; (b) Phase diagram for a single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy in magnetic fields up to 7 T, constructed on the M (T) curves basis (M_s—martensite start temperature; M_f—martensite finish temperature; A_s—austenite start temperature; and A_f—austenite finish temperature; ΔM—the magnetization jump occurring during the magnetostructural transition).

characteristic temperatures of the magnetostructural transition is ±0.6 K. Also, the phase diagram for the single crystal of the $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy was constructed up to a magnetic field of 7 T on the basis of the M (T) curves [Fig. 1(b)]. The sensitivity coefficient of the magnetostructural transition to the magnetic field was determined from the phase diagram, and it is found to be $dT/\mu_0 H = 0.7$ K/T. A positive value of the sensitivity coefficient for the magnetostructural transition is quite a characteristic of Heusler alloys and demonstrates direct MCE in the magnetostructural transition region. Figure 2 shows the results of studies on

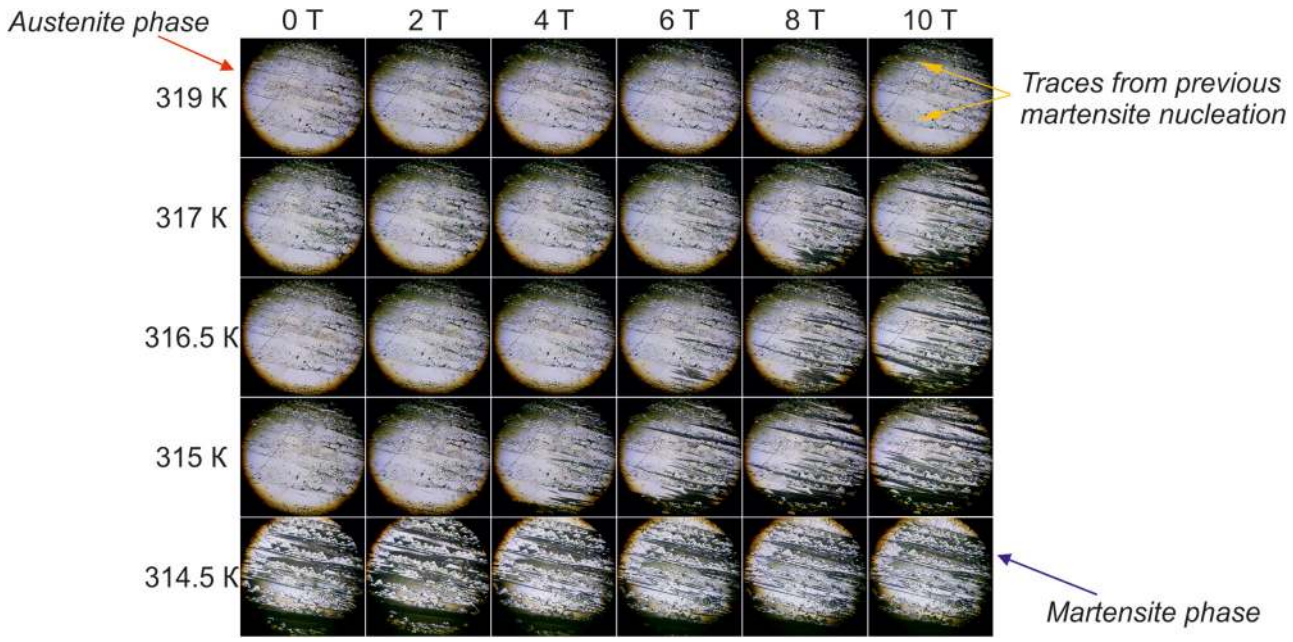

FIG. 2. Formation of martensite on application of magnetic fields up to 10 T in a single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy on cooling without thermal cycling for different initial temperatures of experiment. Frame size is $2 \times 2\ mm^2$.

martensitic twins in a single crystal of $Ni_{2.19}Mn_{0.81}Ga$ alloy exposed to magnetic fields up to 10 T on cooling without thermal cycling at different initial temperatures of the experiment (T_{exp}). From Fig. 2, it is clear that higher the value of T_{exp} as compared to M_s, the larger the magnetic field that should be applied to nucleate the martensitic phase. For example, at $T_{exp} = 319$ K and $\mu_0 H = 10$ T, the magnetic field that is applied is not high enough for the nucleation of martensite. At $T_{exp} = 317$ K, martensite begins to nucleate when the magnetic field ($\mu_0 H$) is only 6 T. On cooling the sample to 314.5 K, the microstructure on the surface of the samples undergoes an abrupt change, which is quite a characteristic of magnetostructural transitions occurring in single crystals. However, when the temperature is 315 K, even a higher magnetic field (10 T) is not adequate to cause complete magnetostructural transition. As can be seen in Fig. 2, at $T_{exp} = 314.5$ K, a major portion of the surface of the sample contains martensite. When the magnetic field is applied and the field strength is increased up to 10 T, it causes a slight increase in the volume fraction of martensite.

The results of the magnetic-field-induced microstructural transition studies carried out on single crystals of the $Ni_{2.19}Mn_{0.81}Ga$ alloy in magnetic fields up to 10 T on cooling with thermal cycling are presented in Fig. 3. As can be seen in Fig. 3, for the nucleation of martensite, higher magnitudes of magnetic field are to be applied. For example, at $T_{exp} = 316.5$ K and on cooling without thermal cycling, the martensitic phase nucleates at a magnetic field ($\mu_0 H$) of 6 T. But on cooling with thermal cycling in a magnetic field ($\mu_0 H$) of 6 T, the austenitic phase is still observed [Fig. 4 lines (b) and (c)]. On the other hand, the nucleation of the martensitic phase occurs at a magnetic field ($\mu_0 H$) of 8 T only. This may be due to the fact that, for experiments that do not involve thermal cycling, after each cycle of the magnetic field, the surface contains residual martensite and structural flaws/discontinuities that are not visible to the naked eye. The presence of residual/retained martensite or structural discontinuities/defects promotes the growth of martensitic twins at lower magnetic fields in the subsequent magnetization/demagnetization cycles of the sample at the designed/intended temperature. As for the residual martensite or structural inhomogeneities that cannot be identified on the surface, can be explained in the light of results discussed in Refs. 13 and 42–44. In these papers, the dependence of the volume fraction of austenite and martensite formed as a function of temperature or magnetic field in Heusler alloys of Ni–Mn–Ga and Ni–Mn–In–Co systems is shown. From Refs. 42–44, it follows that there are such variations when the proportion of one phase is more prevalent. However, a much smaller amount of another phase still remains in the sample. Also, the temperature dependence of the austenitic fraction of the $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ Heusler alloy was determined on the basis of the dependence of magnetization on temperature, $M(T)$, and microstructural changes by microscopic observations.[13] It can be seen that the curves obtained by different methods have a nonessential difference in behavior. However, precisely such a nonessential difference indicates the existence of internal incomplete transformation from one phase to another. While such internal relaxation processes cannot be detected by optical microstructural examination, they can be unraveled by magnetic measurements.[19]

In addition, the obvious difference in the magnetostructural phase transition behavior exhibited by $Ni_{2.19}Mn_{0.81}Ga$ single crystal alloy on thermal cycling is traced to the phase diagram (T–$\mu_0 H$)

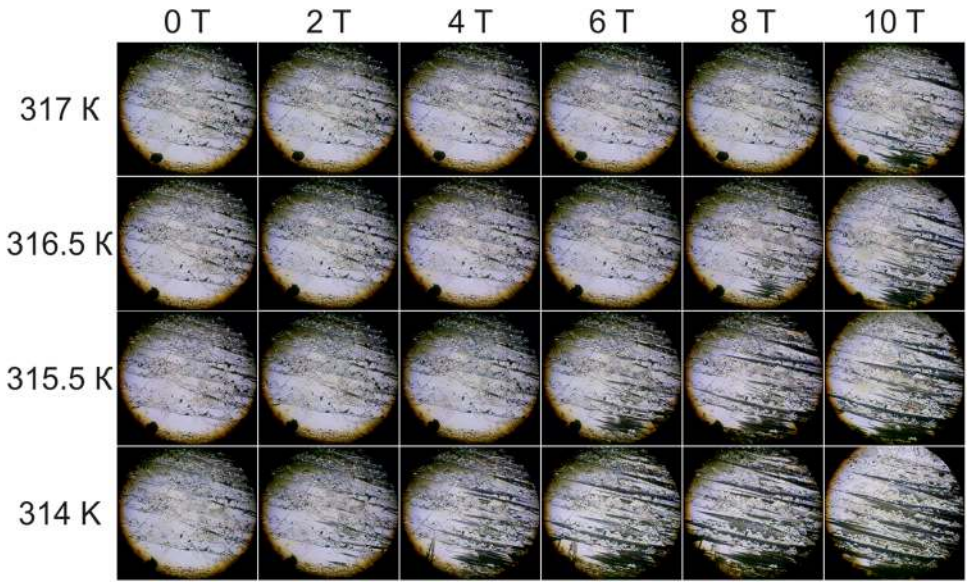

FIG. 3. Formation of martensite on application of magnetic fields up to 10 T in a single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy on cooling after thermal cycling for different initial temperatures of experiment. Frame size is 2 × 2 mm^2.

that is constructed based on the observation of the martensitic twins under the optical microscope on exposure to a magnetic field (Fig. 5). In the figure, the blue line represents the beginning of martensite nucleation on cooling without thermal cycling, while the green line represents the martensite nucleation on cooling after thermal cycling. As can be seen from the phase diagram (T–$\mu_0 H$) for the single crystal $Ni_{2.19}Mn_{0.81}Ga$ alloy, the M_s line for the data representing the experimental condition "cooling after thermal cycling," is higher than that for "cooling without thermal cycling." In other words, after thermal cycling, the nucleation of martensite occurs in higher magnetic fields. However, the sensitivity coefficient of the phase transition remains the same. Thus, the absence of thermal cycling reduces the strength of the magnetic field required for nucleating martensite at the designed temperature. To explain why the transformation undergoes a magnetic field with lower energy at the case of the presence of a residual low-temperature phase (martensitic) and structural discontinuities, let us consider in detail the work of Shamberger and Ohuchi.[45] The thermodynamic behavior of the reversible martensitic phase transition by temperature cycling and partial martensite–austenite transformation of the $Ni_{50.4}Mn_{34.0}Sn_{15.6}$ Heusler alloy in magnetic fields up to 9 T was studied by the researchers.[45] It was demonstrated that both temperature and magnetic field are equivalent driving forces for the phase transition and result in an equivalent hysteresis behavior linked through the magnetic Gibbs free energy. Similarly, in our study, the Ni–Mn–Sn alloy generates only a limited fraction of a new phase under application and removal of magnetic fields up of to 9 T. So, partial transition provides the generation of the amount of the new phase with a smaller field than demanded for the complete transition. The conclusion derived by the authors is

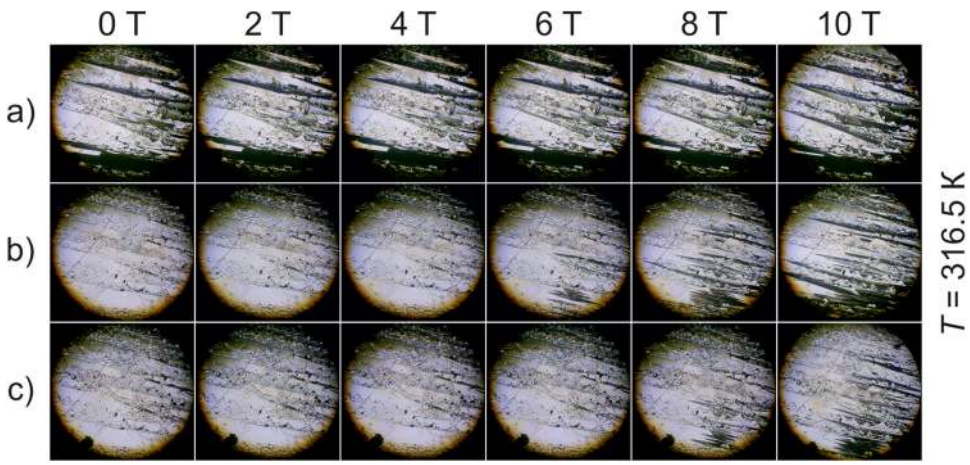

FIG. 4. Formation of martensite on application of magnetic fields up to 10 T in a single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy at T = 316.5 K during (a) heating after thermal cycling, (b) cooling without thermal cycling, and (c) cooling after thermal cycling. Frame size is 2 × 2 mm^2.

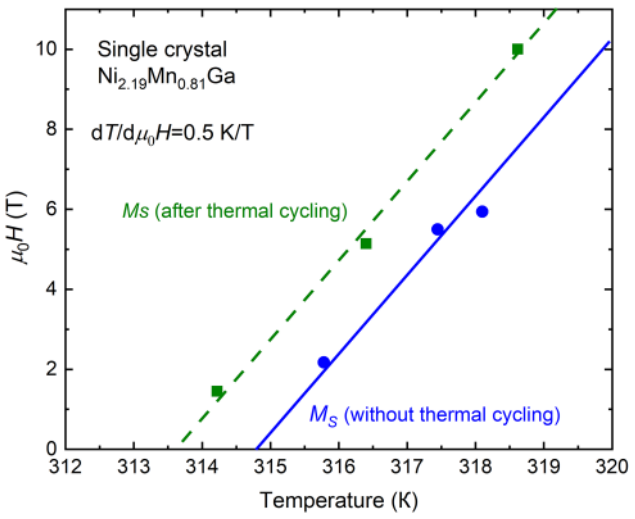

FIG. 5. Phase diagram (T–$\mu_0 H$) for a single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy for fields up to 10 T, both without and after thermal cycling. M_s is martensite start temperature.

still valid not only for the metamagnetic Ni–Mn–Sn alloy, in which martensite is nonmagnetic and austenite is ferromagnetic, but also for the Ni–Mn–Ga Heusler alloy studied in this work. Also direct microscopic observations in high magnetic fields undertaken in this study confirm the validity of thermodynamic treatment of the experiments performed in Ref. 45, which is done by the study of partial thermal hysteresis loops calculating mass fraction of the new phase obtained by magnetization measurement. As compared with a previous study,[45] it is confirmed in the present study that both temperature and magnetic field are equivalent driving forces for the phase transition and result in a similar hysteresis behavior linked through the magnetic Gibbs free energy for the Ni–Mn–Ga Heusler alloys with different types of magnetostructural transition and direct magnetocaloric effect by microstructural observation.

In the case of the single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy, the sensitivity coefficient (k) of the magnetostructural transition to the magnetic field, as determined from the optical microscopic examinations, is 0.5 K/T, which slightly differs from the result ($k = 0.7$ K/T) obtained from magnetic measurements. This may be attributed to the fact that while measuring magnetization, only the magnetic moment of the total sample is investigated.[13] On the other hand, only the surface is studied under optical microscopic examinations. Also, such a difference of the coefficients can be related to the kinetic effects observed in the region of the first order magnetostructural transition, since the magnetic field develops relatively quickly (about 14 T/min) in Bitter coil magnets. The sensitivity coefficient (k) of the martensitic transition to a magnetic field for a polycrystalline $Ni_{2.19}Mn_{0.81}Ga$ alloy is found to be 1 K/T as reported in the relevant literature.[30,40] Accordingly, the magnetostructural transition of a polycrystalline alloy is more sensitive to the magnetic field as compared with the single crystal alloy. The following is an explanation for the difference in behavior that is observed between single crystal and polycrystalline samples for an alloy of the same composition. The $Ni_{2.19}Mn_{0.81}Ga$ alloy in the polycrystalline form has a larger number of crystal defects (for example, grain boundaries) as compared to that in the single crystal form. A polycrystalline sample will, therefore, have a large number of nuclei to form martensite, which, in turn, will lead to a higher sensitivity for the magnetostructural transition to the magnetic field unlike in the case of a single crystal sample.[46] Moreover, the presumption that the larger the number of possible nucleation centers/sites for the formation of martensite, the higher is the sensitivity of the magnetostructural transition to the magnetic field. This is confirmed by the difference observed in the magnetostructural transition under the influence of a magnetic field in the presence/absence of thermal cycling for a single crystal $Ni_{2.19}Mn_{0.81}Ga$ alloy. In the absence of thermal cycling, during the subsequent magnetic induction of martensite after the first cycle of turning on and off of the magnetic field, the alloy already has a residual phase/structural discontinuity, which will act as the nucleation site for the low-temperature phase during subsequent application of the field.

The magnetic-field-induced structure of the single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy under the influence of a magnetic field was studied upon heating and cooling after thermal cycling at different initial temperatures of experiment (T_{exp}) also. In Fig. 4(a), results of experiments conducted in magnetic field up to 12 T and at $T_{exp} = 316.5$ K during heating and after thermal cycling are presented. At $T_{exp} = 316.5$ K, a significant part of the sample surface is occupied by the martensite phase, and further increase in the field causes an increase of martensite fraction. When comparing results at $T_{exp} = 316.5$ K obtained during heating and cooling [Figs. 4(a) and 4(b)], one can clearly see the difference in phase fractions for the same magnetic field. This is explained by the presence of a hysteresis of the magnetostructural transition in a single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy with a first order phase transition. A similar difference of the magnetic-field-induced structural transition behavior on heating, cooling, and partial temperature cycle modes is discussed in Refs. 44 and 47. Konoplyuk *et al.* studied a $Ni_{51.9}Mn_{27}Ga_{21.1}$ Heusler alloy, which is closer to the composition of the alloy from the present work. A characteristic feature of the $Ni_{51.9}Mn_{27}Ga_{21.1}$ Heusler alloy is the presence of two different martensitic structures. For the $Ni_{51.9}Mn_{27}Ga_{21.1}$ alloy, the seven-layered modulated (14M) martensite and the non-modulated (2M) one were found to form on cooling from austenitic phase, while on heating from room temperature, practically a single 2M phase is observed. The influence of the two different martensitic structures is clearly shown in the temperature dependence of the magnetic susceptibility $\chi(T)$ during cooling, heating, and a partial temperature cycle.[44] In each case, $\chi(T)$ has a different behavior. A similar differently behavior of the magnetic-field-induced martensitic transition is observed in this work under different external experimental conditions.

The behavior of magnetic-field-induced microstructural transition, of a $Ni_{2.19}Mn_{0.81}Ga$ single crystal, that does not involve any thermal cycling and the conclusion drawn from additional sites for nucleation of martensite, can directly affect the magnetocaloric effect in the magnetostructural transition region. The value of total isothermal entropy change (ΔS_t) at magnetostructural transition was estimated based on the magnetization [$M(T)$] data obtained

and the phase diagram (T–$\mu_0 H$) constructed. The calculation of ΔS_t was carried out using the Clausius–Clapeyron equation:

$$\frac{dT}{\mu_0 dH} = -\frac{\Delta M}{\Delta S_t}, \tag{1}$$

where $\frac{dT}{\mu_0 dH}$ refers to the sensitivity of the magnetostructural transition and ΔM the magnetization jump occurring during the magnetostructural transition. To calculate the total entropy change ΔS_t, the sensitivity coefficient, $dT/d\mu_0 H = 0.7$ K/T, obtained from the magnetization measurements, was used [Fig. 1(a)]. The jump ΔM was taken as the difference in magnetization at M_s and M_f temperatures [Fig. 1(a)]. The characteristic transition temperatures were determined from the intersections of extrapolations of the magnetization temperature dependence for the corresponding structural phase.

Also, the calculation of the isothermal entropy change ΔS_T was carried out using the magnetization measurements from Fig. 1(a) and the Maxwell equation,

$$\Delta S_T = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right) dH, \tag{2}$$

where M is the magnetization, H is the magnetic field, and T is the temperature. Equations (1) and (2) allow one to determine the value for a specific magnetic field H, while Eq. (1) gives the maximum value of the entropy change caused by the magnetostructural transition. As can be seen from Fig. 6, the ΔS_T value obtained from (2) is much smaller than that obtained from (1), even at a maximum magnetic field of 7 T. The main reason for this difference is that the magnetostructural transition terminates at higher magnetic fields.

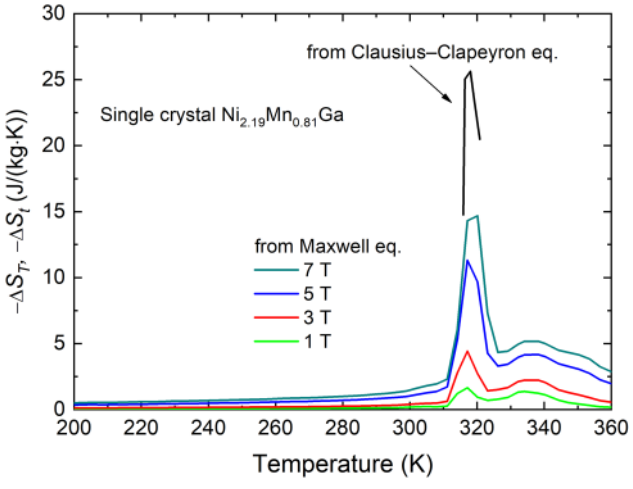

FIG. 6. Temperature dependence of the isothermal entropy change (ΔS_T) for a single crystal of $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy for magnetic fields of 1, 2, 5, and 7 T, respectively. The dark line indicates the plot for total entropy change (ΔS_t) at magnetostructural transition obtained based on the Clausius–Clapeyron equation.

Thus, as can be seen from Fig. 6, the maximum value for the isothermal entropy change as calculated from the equation is $\Delta S_t = 25.6$ J/(kg K). As can be observed from the martensitic twins formed, the presence or absence of thermal cycling does not affect the sensitivity ($k \approx 0.5$ K/T, Fig. 5) of the magnetostructural transition to the magnetic field. Correspondingly, an MCE decrease with sequential sample cycling in a magnetic field, as previously observed in Ref. 30 for a polycrystalline $Ni_{2.19}Mn_{0.81}Ga$ alloy in the magnetostructural transition region, can be associated with a decrease in magnetization jump (ΔM). In turn, the magnetization jump decreases due to the presence of residual martensite after the first magnetic field turn-on. Subsequent magnetic field turn-on increases the volume fraction of residual martensite only, i.e., with each subsequent cycle, the transition from austenite to martensite occurs in increasingly smaller volumes. This leads to a decrease of the MCE during sequential cycling in a magnetic field.

IV. CONCLUSIONS

The thermoelastic martensitic transition in the single crystal $Ni_{2.19}Mn_{0.81}Ga$ Heusler alloy under the influence of high magnetic fields up to 10 T under isothermal conditions was studied using an indigenously developed optical microscope. A phase diagram (T–$\mu_0 H$) between the magnetic field and temperature was constructed up to a field of 10 T based on the microstructural observations of the alloy studied. It is shown that the dependence of the first order phase transition characteristic temperatures on the magnetic fields of up to 10 T shows a linear relationship with a corresponding slope coefficient of 0.5 K/T. It is also established that the absence of thermal cycling reduces the magnitude of magnetic field that is required to cause nucleation of martensite since the residual martensite acts as an additional nucleating point for the formation of martensite. The main reason for the decrease of the MCE in the magnetostructural transition region during sequential cycling in a magnetic field is the decrease in magnetization jump caused by residual martensite, which is formed as a result of the first magnetization. Subsequent turning-on of the magnetic field causes an increase in the volume fraction of residual martensite, i.e., with each subsequent cycle, the transition from austenite to martensite occurs in increasingly smaller volumes.

ACKNOWLEDGMENTS

The work was carried out within the framework of state task, President of Russian Federation (Grant No. MK-355.2020.2), and was partially supported by the Russian Foundation for Basic Research (Project No. 20-58-54006). One of the authors (V.K.), gratefully acknowledges partial support by Act 211 Government of the Russian Federation (Contract No. 02.A03.21.0011).

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