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Formation of a Martensitic Twins Structure in $Ni_{2.16}Mn_{0.84}Ga$ Heusler Alloy by High Magnetic Fields under Adiabatic and Isothermal Conditions

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Abstract—The results are presented from experimental studies of the formation of martensitic twin structures in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy under the effect of magnetic fields of up to 14 T using a specially developed optical microscope under isothermal and adiabatic conditions. A qualitative model is proposed that explains the differences between the progress magnetoinduced magnetostructural first-order phase transitions under different thermodynamic conditions.

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INTRODUCTION

Studies of materials that experience magnetic and structural phase transitions (PT) have attracted growing attention in recent years, due to the high interest in creating alternative solid-state mechanical devices and energy systems. Among the most interesting of these materials are Heusler's families of Ni–Mn–X alloys (X = Ga, In, Sn, Sb), in which numerous bright physical effects (e.g., the direct and reverse giant magnetocaloric effects (MCEs) and the magnetic memory of shape) have been observed [1–9]. It is known [10] that the main contribution to the giant MCE comes from magnetic and structural subsystems. However, the nature of the interaction between solid-state structural and magnetic subsystems during PTs in magnetic fields remains poorly studied. As a consequence, there are no reliable theoretical models that allow us to predict the technical parameters of materials for possible practical devices.

Direct studies of magnetoinduced thermoelastic structural martensitic transformations are hampered by the need to use strong magnetic fields and the absence of standardized techniques. For example, studies of structure in strong magnetic fields cannot be conducted by means of electron, X-ray, or neutron diffraction. The most convenient and productive direct approach to such studies is to observe the magnetically-induced evolution of martensitic twins using an optical microscope. Heusler Ni–Mn–Ga alloys experiencing the direct MCE were studied in this manner in [11, 12]. The formation and disappearance of martensitic twins in a magnetic field were studied for samples with the reverse MCE using Ni–Mn–In samples with pulses of up to 31 T [14] and stationary fields as strong as 1.1 T [15]. A magnetic field value of 1.1 T is not sufficient for the total completion of a structural transition, and the use of pulse fields does not allow us to study in detail first-order PTs, due to the brief duration of the pulse field. The authors of [15] therefore proposed an experimental procedure for studying the structure of Heusler alloys on the microscopic level in the magnetic field of a Bitter magnet. This requires simultaneous observation of the formation (or disappearance) of martensitic twins on the surface of a sample using an optical microscope while measuring the local temperature. This approach allows us to study magnetoinduced thermoelastic phase transitions in the in situ mode by optical means under different thermodynamic conditions.

The Heusler alloy $Ni_{2.16}Mn_{0.84}Ga$, which experiences the direct MCE in the region of the martensitic phase transformation, was chosen as the object of study. This alloy is part of the family of $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys [1–5]. A sequence of interacting PTs is observed in the alloys of this family: a second-order magnetic transition of the paramagnet–ferromagnet type, and a thermoelastic martensitic structural first-order PT from the cubic phase (austenite) to the low-temperature, low-symmetry phase (martensite). A strict dependence of PT temperatures

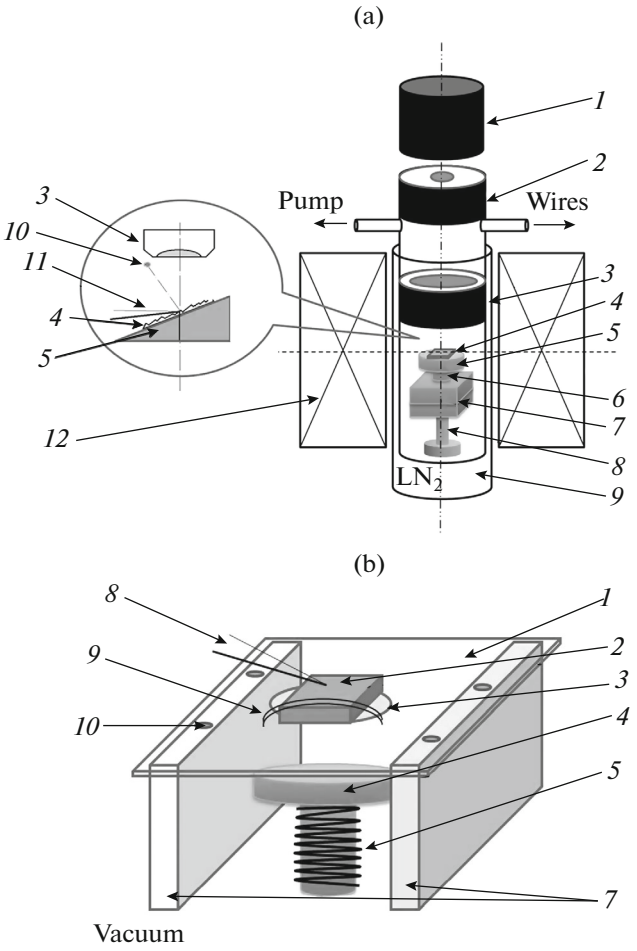

Fig. 1. (a) Basic scheme of the optical microscope for studying the surface of metallographic cross sections of Heusler alloy in the field of a Bitter electromagnet; (b) system for holding the sample when conducting experiments under adiabatic conditions.

on composition is characteristic of these alloys [1–5]. When $x < 0.17$, the martensitic transition occurs in the ferromagnetic state; when $x > 0.26$, it occurs in the paramagnetic state. The merging of transitions into a single magnetostructural first-order PT from paramagnetic austenite to ferrimagnetic martensite is characteristic of the interval $0.17 < x < 0.26$.

It is known that the saturation magnetization of the $Ni_{2.16}Mn_{0.84}Ga$ alloy's martensite (the low-temperature phase) is greater than that of austenite (the high-temperature phase). According to the Le Chatelier–Brown principle, this expands the region of stability of the low-temperature phase in an external magnetic field and raises the temperatures of the martensitic first-order PT. At a constant temperature near the PT in the austenitic phase, the switching on of a fairly strong magnetic field results in nucleation of the martensitic phase, accompanied by the emergence and growth of martensitic twins. This process is reversible, and the martensitic twins disappear when the magnetic field is switched off [6]. Under adiabatic conditions, the nucleation of the low-temperature structural phase in a magnetic field is accompanied by a rise in the alloy's temperature. This effect is conventionally referred to as the giant MCE. The physical importance of this effect is that the strongly magnetic martensitic phase formed in a magnetic field has less internal energy than the initial, austenitic phase. As a result, under adiabatic conditions, when external heat cannot flow into a sample, a new phase is formed with a higher temperature than the initial phase.

A reversible PT also occurs under isothermal conditions, but it proceeds in a different manner: At the constant temperature of the sample set by the thermostat, the sample can exchange energy with the external medium. The switching on of the magnetic field and the emergence of the low-temperature phase under isothermal conditions is accompanied by a release of heat from the sample to the thermostat. The switching off of the field is accompanied by the absorption of heat from the surrounding medium into the sample. These processes were studied in this work via simultaneous direct optical observation of the formation of a new structural phase in a magnetic field upon a change in sample temperature.

EXPERIMENTAL

As noted above, a sample of $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy was chosen as the object of study. The alloy was manufactured by means of cold-hearth arc melting. Heat treatment of the alloy consisted of annealing at 1073 K for 48 hours in vacuum with subsequent cooling in the furnace [1, 4].

The characteristic temperatures of the beginning and end of the direct and reverse first-order PTs were determined for the $Ni_{2.16}Mn_{0.84}Ga$ sample using results obtained via differential scanning calorimetry (DSC): $M_s = 310$ K, $M_f = 302$ K, $A_s = 307$ K, $A_f = 320$ K. According to data from magnetic measurements, the Curie point was $T_C = 339$ K.

Figure 1a shows the basic scheme of the experimental device developed by the authors of this work at the International Laboratory of High Magnetic Fields and Low Temperatures (Wrocław, Poland). The device is designed to observe the formation of the relief of martensitic twins on the surfaces of samples polished in the austenitic state with simultaneous recording of the sample's temperature and the patterns of twins formed upon the direct martensitic transition in fields of a Bitter electromagnet of up to 14 T, using a video camera [13].

The device includes an optical microscope made of nonmagnetic materials. It consists of the basic optical system of an ocular and lenses *2* and *3*, and a thermostat chamber. Vacuum (10^{-4} Torr) is maintained in the working chamber using a vacuum pump. Sample *4* polished in austenite is placed on the surface of work-

ing table *5* in the thermostat chamber. The sample is illuminated using LED *10*, which is fastened to a flexible strip of copper that allows us to change the angle of incidence of light rays onto the surface of the sample. Using this system, one can select the best direction of the light beams and obtain the maximum contrast of the relief on the reflecting surface of a sample with twins. The temperature of the sample is fixed using a nichrome heater wound in two wires on sample holder *6*. Specially made Dewar flask *9* containing liquid nitrogen is used for measurements at lowered temperatures.

Adiabatic or isothermal conditions for performing an experiment are created as a result the physical properties of the working table, on which a sample is placed. To perform an experiment under isothermal conditions, working table *5* made from brass with high thermal conductivity is used. For better thermal contact, the sample is glued on using a heat-conducting silver paste. Note that the mass of the working table is orders of magnitude greater than that of the sample, ensuring that the temperature during observation remains nearly constant.

To perform an experiment under adiabatic conditions, a specially made holder is used. It allows us to achieve minimal thermal contact between a sample and the device while guaranteeing the mechanical stability of the plane of the sample in the external magnetic field. Both holders are placed (separately) on the two-coordinate positioning system of sample *7*. This system lets us move the sample in the plane perpendicular to the optical axis of the microscope. The sample is displaced along the optical axis of the microscope (brought into focus) using screw *8* in the base of the positioning system.

The scheme in Fig. 1b shows an external view of the system for fastening the sample under adiabatic conditions. Sample *2* is fixed by thread *9* to fabric *1*, which is in turn stretched over Teflon holder *7* using screws *10*. Hole *3* in fabric *1* lies under the sample to reduce sample–fabric contact. Details *1*, *3*, *7* are made of materials whose thermal conductivity is an order of magnitude less than that of the metallic sample. The sample is heated using nichrome heater *5* wound in two wires on brass cylinder *4*. Cylinder *4* provides an even flow of heat, due to thermal radiation. The temperature is fixed using thermocouple *8*, glued directly onto the surface of the sample with silicate adhesive.

The experiments were performed using a water-cooled Bitter electromagnet [13] capable of producing stationary magnetic fields of up to 14 T. Expanding the range of the magnetic field to 14 T allowed us to observe the emergence and annihilation of the martensitic structure during the reversible first-order PT along the field. The ability to compare the magnetoinduced change in the sample's temperature while visualizing the evolution of the structure under the action of the magnetic field allows us to analyze the effect of the change in the sample's structure during the MCE near the martensitic transition.

The device functions in the following manner. After the temperature of the experiment is stabilized, Bitter electromagnet *12* is switched on (Fig. 1a). Images of the sample's surface are recorded using video camera *1*. The sample temperature is measured using copper–constantan thermocouple *11*, the end of which is placed directly on sample surface *4*. Signals from the thermocouple and the magnetic field sensor arrive at Keithley 2000 multimeters. All measuring instruments are are connected to one another and to a computer by a GPIB bus. For the synchronous recording of the video, temperature, and parameters of the magnetic field, the specially developed program was used.

RESULTS AND DISCUSSION

Measurements are made according to the following protocol. The required value of sample temperature T_{start} is first set (e.g., $T_{start} > M_s$, i.e., above the point of the onset of the transition to the martensitic phase). The magnetic field is then switched on. The magnetic field of the required value induces the first-order PT. The nucleation and magnetoinduced evolution of martensitic twins on the polished surface of the sample is recorded using video camera *1* located above the ocular of the microscope. The key factor is initial temperature T_{start} of the experiment: the greater the difference $(T_{start} - M_s)$, the stronger the magnetic field needed for initiating and fully terminating the structural transition.

Figure 2 shows a series of micrographs reflecting the evolution of the martensitic PT in the sample of the $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy at different initial temperatures under the action of a magnetic field varied from 0 to 14 T. It can be seen that the greater the difference between temperatures $(T_{start} - M_s)$, the stronger the magnetic field needed for the nucleation of the martensitic phase. For example, at $T_{start} = 312$ K the nucleation of the martensitic phase occurs only in a magnetic field stronger than 10 T. A field of 14 T is not sufficient for the full termination of the first-order PT at the given temperature. It can be seen from micrographs from our micrographs that the formation of the martensitic domain structure at the temperature of 308 K starts in a magnetic field of around 3 T. With a further increase in the magnetic field, the volume of the martensitic domains grows. Raising the magnetic field to 10 T finally produces the martensitic phase. If the initial temperature of the experiment lies in the interval of the hysteresis temperature (e.g., $T_{start} = 306$ K), the prehistory of the experiment is important. If temperature T_{start} is reached while heating (i.e., the previous experiment was performed at a lower T_{start}), martensite will result. If temperature T_{start} is reached while cooling (i.e., T_{start} of the previous experiment was higher), the sample will be predominantly in the aus-

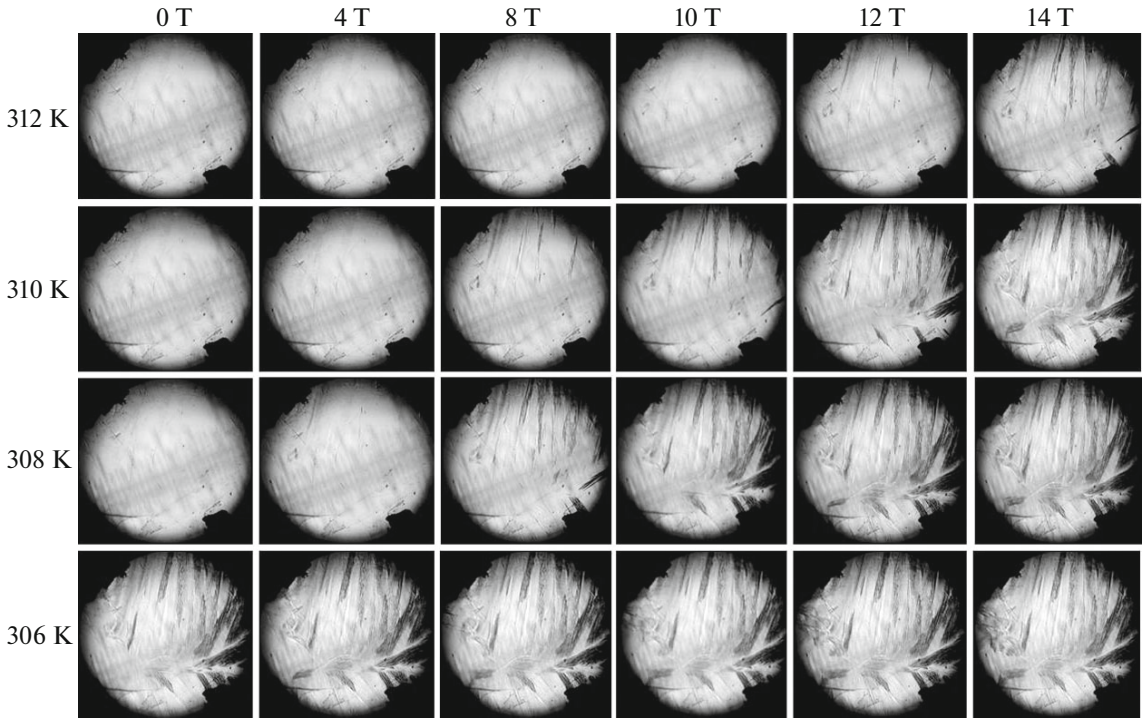

Fig. 2. Formation of the structure of martensitic twins under the action of a magnetic field in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy at different initial temperatures T_{start} of an experiment, established after cooling under isothermal conditions. The frame size is 2×2 mm^2.

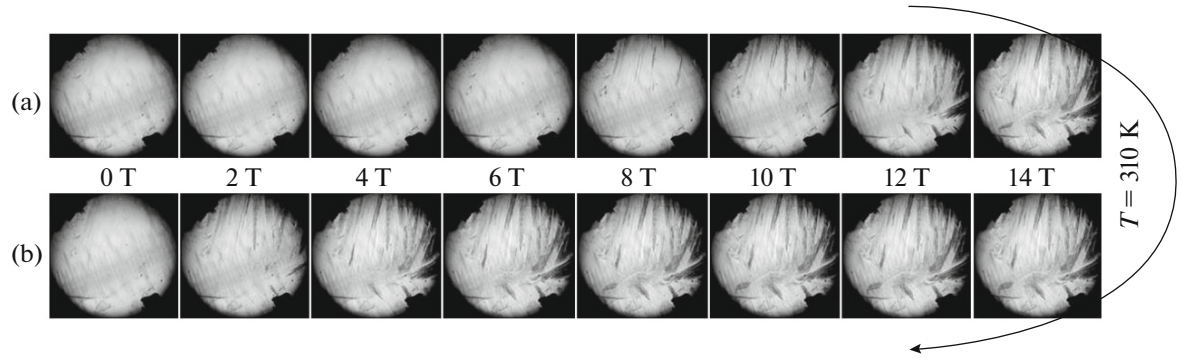

Fig. 3. Reverse magnetoinduced structural transition in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy under isothermal conditions at a temperature of 310 K, established after heating the sample. (a) The magnetic field increases from 0 to 14 T; (b) the magnetic field decreases from 14 to 0 T. The frame size is 2×2 mm^2.

tenitic phase, and switching on the magnetic field will irreversibly transform it into martensite.

Let us consider in detail the formation of the martensitic structure under the action of a magnetic field at initial temperature $T_{start} = 310$ K (Fig. 3). The micrographs in Fig. 3a correspond to raising the magnetic field from 0 to 14 T; the micrographs in Fig. 3b, to lowering it from 14 to 0 T. A magnetic field of around $\mu_0 H = 4$ T is sufficient to initiate the first-order PT at a constant $T_{start} = 310$ K. A further increase in the magnetic field raises the volume fraction of the martensitic phase in the sample, and the structural transition is almost fully terminated in a magnetic field of $\mu_0 H = 11$ T. Reducing the magnetic field to around $\mu_0 H = 4$ T results in a reverse martensite–austenite structural transition. Upon reaching $\mu_0 H = 0$ T, the sample transitions fully to the austenitic state, testifying to the reversibility of the magnetoinduced magnetostructural first-order PT in the $Ni_{2.16}Mn_{0.84}Ga$ sample under isothermal conditions at a constant $T = 310$ K.

The (T–H) phase diagram was plotted using optical observations of a magnetoinduced first-order PT

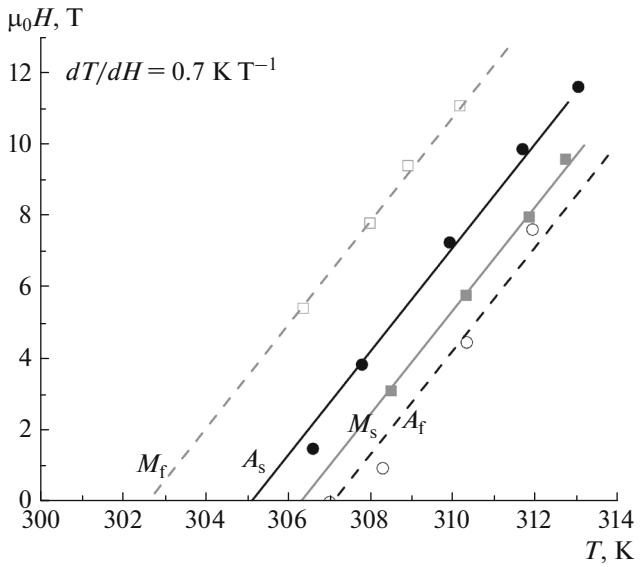

Fig. 4. (T–H) phase diagram of $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy.

in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy (see Fig. 4). The sensitivity of the structural transition to the magnetic field in the $Ni_{2.16}Mn_{0.84}Ga$ alloy was around $dT/dH = 0.7$ K T^{-1}.

As was noted above, the magnetostructural transition's contribution to the MCE comes from a sample's structural and magnetic subsystems. The MCE is defined as the heat coming into or leaving a sample via the surrounding medium under isothermal conditions. It is measured either in units of kJ kg^{-1} upon a change in the sample's temperature under adiabatic conditions, or in units of K upon a change in the external magnetic field [9, 16]. The experiments to study magnetoinduced structural PTs in samples of $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy under the action of a magnetic field were therefore performed under different thermodynamic conditions (in the isothermal and adiabatic modes). For comparison, Fig. 5a shows video frames of a magnetically-induced martensitic PT at initial temperature $T_{start} = 310$ K upon heating under isothermal conditions; Fig. 5b shows the same under adiabatic conditions. In the experiment under adiabatic conditions, the volume of the magnetoinduced martensite differs substantially from the one during the first-order PT under isothermal conditions. It can be seen that the growth of the martensitic phase is hampered in the adiabatic mode.

A qualitative model for explaining the differences between the formation of the martensitic phase during experiments under isothermal and adiabatic conditions is shown in Fig. 6. It can be seen from the figure that under isothermal conditions ($\Delta S \neq 0$, $\Delta T = 0$), the sample transitions from state *1* to state *2* upon an increase in magnetic field induction. For the full termination of the first-order PT, the magnetic field must reach a nominal value of $\mu_0 H_{1-2}$. The temperature of the sample changes during the structural transition under adiabatic conditions ($\Delta S = 0$, $\Delta T \neq 0$). As a result, the magnetoinduced first-order PT will follow course *1–3*. The magnetic field must reach a nominal value of $\mu_0 H_{1-3}$ for the martensitic transition to be fully terminated. It can be seen from the qualitative model that $\mu_0 H_{1-3} > \mu_0 H_{1-2}$. This indicates that under adiabatic conditions, a stronger magnetic field is needed for a full first-order PT than under isothermal conditions. This is clearly demonstrated as well by optical observations of structural transitions under the action of a magnetic field. At the same value of the magnetic field, the ratio of the martensitic phase in the sample is less under adiabatic conditions than under isothermal conditions. The linear extrapolation (*1–3*) in Fig. 6 yields the magnitude of the field ($\mu_0 H_{1-3} \sim 21$ T) needed for a reversible martensitic PT in $Ni_{2.16}Mn_{0.84}Ga$ alloy under adiabatic conditions at an initial temperature of 310 K.

Based on direct observations of a magnetoinduced first-order PT in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy, different courses of structural transitions in the adiabatic and isothermal modes were demonstrated. It is possible to conclude that one must consider these features in order to achieve the most effective thermodynamic cycles (e.g., the Carnot cycle) in promising magnetic refrigerators and heat pumps, since the observed dif-

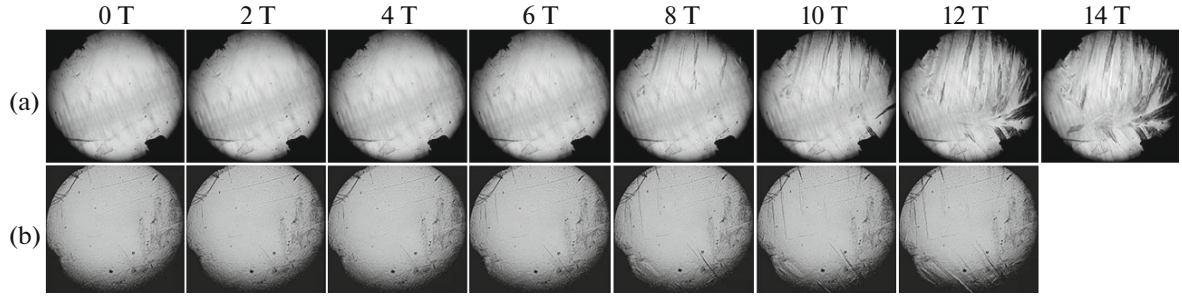

Fig. 5. Magnetoinduced martensitic transition in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy under (a) isothermal and (b) adiabatic conditions at $T_{start} = 310$ K.

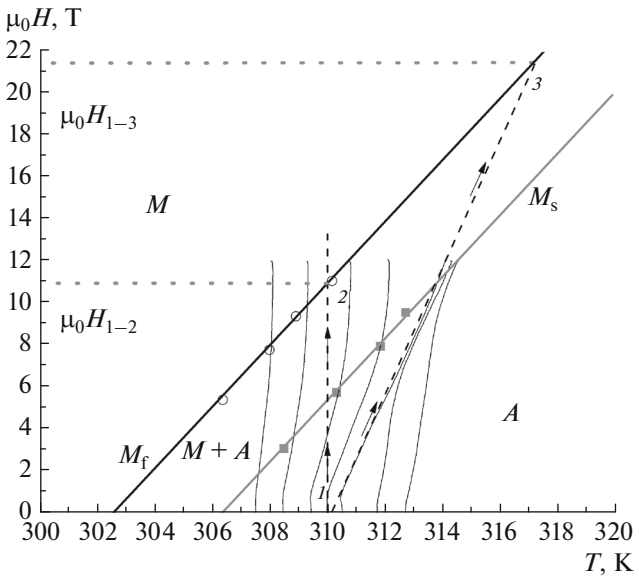

Fig. 6. Qualitative model of the course of the first-order PT in $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy. Line (*1–2*) shows the course of the change in the structure of the sample under isothermal conditions. Line (*1–3*) shows its extrapolation, plotted using the curve of the change in the temperature of the sample under adiabatic conditions (initial temperature, 310 K). The fine curves in the plot show the experimental change in the temperature of the sample under adiabatic conditions at different initial temperatures.

ferences between the field characteristics of magnetoinduced PTs in different modes are substantial. The experimental data should stimulate theoretical works to quantitatively describe the observed dependences.

CONCLUSIONS

Using a specially developed optical microscope, the formation of the martensitic structure of the $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy under the action of magnetic fields of up to 14 T in the adiabatic and isothermal modes was studied. The (T–H) phase diagram of the martensitic first-order PT was plotted for $Ni_{2.16}Mn_{0.84}Ga$ Heusler alloy. It was shown that the dependence of the characteristic temperatures of a first-order PT on the magnetic field is linear with the coefficient 0.7 K T^{-1}. The formation of the martensitic structure under isothermal and adiabatic conditions was studied. It was found that under adiabatic conditions, a much stronger magnetic field is required for a reversible PT than under isothermal conditions. A qualitative model was proposed that explains the difference between the courses of magnetoinduced first-order PTs under different thermodynamic conditions. A wide variety of materials with direct and reverse giant MCEs and magnetoinduced martensitic PTs can be studied using the proposed direct technique.

ACKNOWLEDGMENTS

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