

# Thermal diffusivity and thermal conductivity of Ni<sub>53.6</sub>Mn<sub>27.1</sub>Ga<sub>19.3</sub> shape memory alloy

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## Abstract

The temperature dependence of the thermal diffusivity, specific heat and density were determined experimentally, and the thermal conductivity was obtained as a product of these parameters in the temperature range from 300 to 650 K for the polycrystalline shape memory Ni<sub>53.6</sub>Mn<sub>27.1</sub>Ga<sub>19.3</sub> alloy. The phase transformation martensite → austenite took place at about 450 K. The thermal diffusivity and thermal conductivity of the martensite was about 40% lower than that of the austenite. Thermal diffusivity was measured by the flash method where the time dependence of the temperature rise after irradiation was also determined. The latent heat of the phase transformation substantially lowers the temperature rise after irradiation in the transient temperature range.

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**Keywords:** Thermal diffusivity; Thermal conductivity; Latent heat; Shape memory alloys; Martensitic phase transformation

## 1. Introduction

For high-temperature applications of the solids, the temperature dependences of various physical parameters are investigated. There are no problems with the measurement of these parameters in most cases. Problems can occur when the physical properties are studied in the temperature region of the first-order phase transformation where the latent heat can be an important factor in influencing measured data.

At present attention is focused on shape memory materials. The shape memory effect is based on the martensite ↔ austenite phase transformation, which is a first-order phase transformation. Although much attention has already been paid to this phase transformation a problem of mutual influencing of the phase transformation and thermal conductivity has not yet been resolved.

For the general case of heat flow in three dimensions, in a homogenous and isotropic material the equation of heat conduction is given as:

$$\frac{dT}{dt} = \frac{\lambda}{\rho c_p} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (1)$$

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where  $T$  is temperature and  $t$  is time. The term  $\lambda/\rho c_p$  ( $\lambda$  is the thermal conductivity,  $\rho$  is the density and  $c_p$  is the specific heat) was defined the thermal diffusivity by Lord Kelvin. This equation may be solved only for the given initial and boundary conditions.

The solutions of the temperature distribution for a large number of relatively simple shapes and boundary conditions can be found in Carslaw and Jaeger [1]. Numerous methods of measurement of thermal diffusivity and thermal conductivity are based on them. The accuracy of the measurement of the thermal diffusivity and thermal conductivity then depends on the experimental realization of initial and boundary conditions required for the solution of the heat conduction equation. One of basic conditions of the derivation and solution of the heat conduction equation is that all thermophysical parameters in Eq. (1) are not dependent on temperature. Generally they depend on temperature but to a good approximation it is assumed that they are a function only of the local material and state. However in the temperature range where phase transformations occur the thermophysical parameters dramatically change with temperature. Non-fulfilling of the boundary conditions may lead to wrong conclusions at the interpretation of the thermal conductivity results. Careful analysis of the heat

conduction in such systems is necessary before a physical interpretation of results is made.

$\text{Ni}_2\text{MnGa}$  alloy is a promising high-temperature shape memory alloy, which has an excellent shape memory effect and high thermal stability. The alloys with martensitic transformation above room temperature are of potential technical interest because they have shown phase transformations at useful operation temperatures. Although extensive research on this alloy has been conducted and been written about (for example [2–4]), research and the study of thermal diffusivity and thermal conductivity is practically absent. Both parameters can be important not only for the research of these alloys but also for applications (optimum preparation, heat treatment and so on).

The systematic study of the thermal properties of polycrystalline  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  ( $x = 0, 0.04, 0.6, 0.10, 0.14, 0.18$  and  $0.24$ ) can be found in the work of Kuo et al. [5]. Transport properties including electrical resistivity, specific heat, Seebeck coefficient and thermal conductivity were investigated up to  $T = 400$  K. All these physical properties were very sensitive to the structural and magnetic transformations. Similar results were obtained in the work of Kreissel et al. [6] where the electrical resistivity and the specific heat were studied. The work of Cesari et al. [7] shows only minor sensitivity to temperature variations for specific heat during phase transformation in single-crystal samples.

The thermal conductivity investigated by Kuo et al. [5] exhibits a step-like jump accompanied by a remarkable spike-shaped peak at the temperature range around the martensitic transition temperature. A similar peak features in the temperature dependence of thermal conductivity were also found in materials that undergo a Peierls transformation at low temperatures [8–10]. The appearance of a Kohn anomaly and the anomalous heat carried by soft phonons were suggested as possible origins for such peaks in the thermal conductivity.

The main aim of this paper is to determine and to analyze the temperature dependence of the thermal diffusivity and the thermal conductivity of the polycrystalline shape memory  $\text{Ni}_{53.6}\text{Mn}_{27.1}\text{Ga}_{19.3}$  alloy. Analysis of results will be focused on the transient temperature range.

## 2. Experimental part

A polycrystalline ingot of  $\text{Ni}_{53.6}\text{Mn}_{27.1}\text{Ga}_{19.3}$  alloy was prepared by arc melting the pure elements under argon atmosphere. The samples prepared from the ingot were annealed for 4 days at 1123 K.

Samples for the thermal diffusivity measurements had a diameter of 16 mm. The measurements of the thermal diffusivity were performed in the temperature range 300–650 K in an argon atmosphere using the flash method described elsewhere [11]. The front of the sample was irradiated by a short energy pulse from a Xe-flash lamp and the time dependence of the temperature rise was determined on the opposite side of the sample. The thermal diffusivity was obtained from the half time (this is the time when half of the maximum temperature rise is reached) and the thickness of the sample.

The measurement of each experimental point of the temperature dependence was performed during heating after 10 minutes hold at the test temperature; the time of the measurement was also 10 minutes. The surface of the sample was blackened by graphite. The accuracy of the measurement was checked by measuring the thermal diffusivity of an Armco iron sample (Armco iron is a standard material for the measurement of the thermal diffusivity and conductivity). The difference between measured and tabulated values [12] is about  $\pm 3\%$ .

The temperature dependence of the density was calculated from the density measured at 20 °C by weighing the sample in rectified and dried toluene ( $\rho_o$ ) and from respective values of thermal expansion data by the relation:

$$\rho = \rho_o \left(1 + \frac{\Delta l}{l_o}\right)^{-3} \quad (2)$$

where  $\Delta l/l_o$  is the relative elongation. This parameter was determined using the Netzsch 402E dilatometer in argon atmosphere. The thermal conductivity was calculated using the thermal diffusivity, the specific heat and the density.

## 3. Results and discussion

The temperature dependence of the thermal diffusivity for the  $\text{Ni}_{53.6}\text{Mn}_{27.1}\text{Ga}_{19.3}$  alloy is shown in Fig. 1. The figure clearly shows an increase of the thermal diffusivity at  $T \sim 450$  K, where the phase transformation martensite  $\leftrightarrow$  austenite occurs. The thermal diffusivity of austenite is about 40% higher than that of the martensite (the values before and after phase transformation were compared, and it increases with increasing temperature faster than that for the martensite. A small peak below  $T = 370$  K demonstrates a phase transformation of the ferromagnetic martensite to the paramagnetic martensite. This temperature was found as transition temperature for magnetic phase transformation by magnetic measurements using a PPMS device of Quantum Design Company (USA). The temperature dependence of the thermal diffusivity has a shape

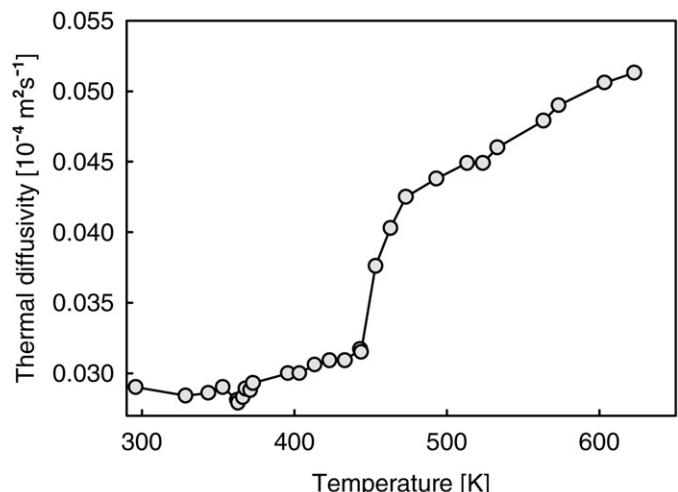


Fig. 1. Temperature dependence of the thermal diffusivity (distance of the flash lamp from the sample was 190 mm).

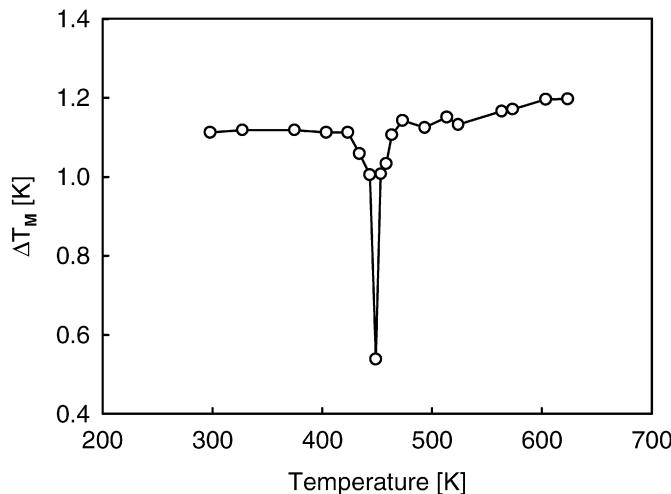


Fig. 2. Temperature dependence of the temperature rise  $\Delta T_M$  after irradiation (distance of the flash lamp from the sample was 190 mm).

of a reverse peak characteristic for this type of phase transformation (see iron in Ref. [12]). The temperature dependence of the maximum temperature rise after irradiation of the sample is shown in Fig. 2 (the distance of the flash lamp from the sample was 190 mm). It can be seen from both figures that the thermal diffusivity as well as the temperature rise change significantly at the transformation temperature. When the transformation temperature is reached in a sample after irradiation, the phase boundary between the austenite and the martensite propagates through the sample. The heat conduction and the phase transformation propagate together. The energy balance at the interface is then [13]

$$-\lambda_A \left( \frac{\partial T}{\partial x} \right)_A = u \rho H - \lambda_M \left( \frac{\partial T}{\partial x} \right)_M \quad (3)$$

where  $-\lambda_A \left( \frac{\partial T}{\partial x} \right)_A$  is the heat flux into the austenite at the interface,  $u \rho H$  is the latent heat absorption rate and the last term  $-\lambda_M \left( \frac{\partial T}{\partial x} \right)_M$ , is the heat conducted away from the moving interface into the martensite. The term  $u$  is the interface velocity,  $\rho$  is the density (it is assumed that the density in both phases are the same) and  $H$  is the latent heat per unit mass. The interface velocity  $u$  and temperature are time dependent.

Knowledge of the specific heat and the density is necessary for the determination of the thermal conductivity from the thermal diffusivity. In the literature we can find several studies concerning the measurement of the specific heat of Ni–Mn–Ga based alloys. Kreissl et al. [6] have shown that the specific heat of the polycrystalline  $\text{Ni}_2\text{MnGa}$  alloy depends on the thermal history of the alloy. The peak in the transition temperature range was found only in the alloy quenched from  $T = 1273$  K but not after quenching from  $T = 1073$  K. Cesari et al. [7] presented no changes of the specific heat during the phase transformation for two single crystals of the non-stoichiometric Ni–Mn–Ga alloys. Their results were obtained using an AC calorimeter. Small peaks on the temperature dependence of the specific heat measured also by AC calorimeter were found in [5], and the lambda type of peak for  $\text{Ni}_2\text{MnGa}$  was presented in [14]. Fraile-Rodrígues et al. [15] made an analysis of the measurement of the

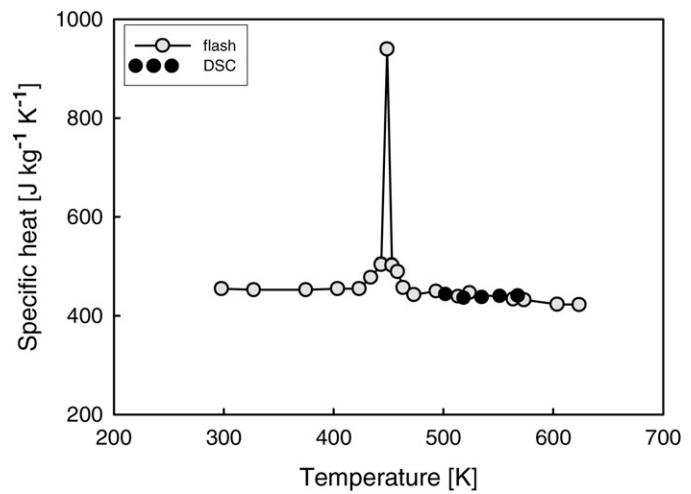


Fig. 3. Temperature dependence of the specific heat.

the specific heat and they have shown that the AC technique does not allow the measurement of the latent heat associated with a first order phase transformation.

In the present work the specific heat was obtained by the flash method. For a determination of the specific heat by this method the following relation is used [16]:

$$c_p = \frac{Q}{\rho L \Delta T_M} \quad (4)$$

where  $Q$  is the energy input per unit area,  $\Delta T_M$  is maximum temperature rise after irradiation and  $L$  is the sample thickness.

The knowledge of the  $Q$  value is not necessary for the determination of the thermal diffusivity by the flash method [17]. The  $Q$  value for the determination of the specific heat was obtained indirectly from the specific heat determined in the differential scanning calorimeter, Perkin Elmer Pyris Diamond DSC, at room temperature and using relation (4). This value was then used for the determination of the temperature dependence of the specific heat from the maximum temperature rise (distance of the flash lamp from the sample was 190 mm) measured in our flash apparatus (Fig. 2). No correction for the radiation losses was made. The result is shown in Fig. 3. Good agreement between these values of specific heat and the specific heat determined in DSC for the austenite (above the transition temperature) can be seen from this figure. Changes of the specific heat during the magnetic transformation were not found by this method.

The density is a further parameter necessary for the determination of the thermal conductivity. The temperature dependence of the density is shown in Fig. 4. The temperature dependence of the relative elongation used for the calculation of the density is displayed in Fig. 5. It can be seen that only a small deformation change occurs at the phase transformation.

For our measurement, a polycrystalline material was used with the equiaxed structure where only small structure anisotropy exists. The dilatation characteristics shown in Fig. 5 were obtained using a heating rate of 0.5 K/min. The transformation temperature (this is the temperature for which the rate of transformation is highest) was  $T = 452$  K. The transformation

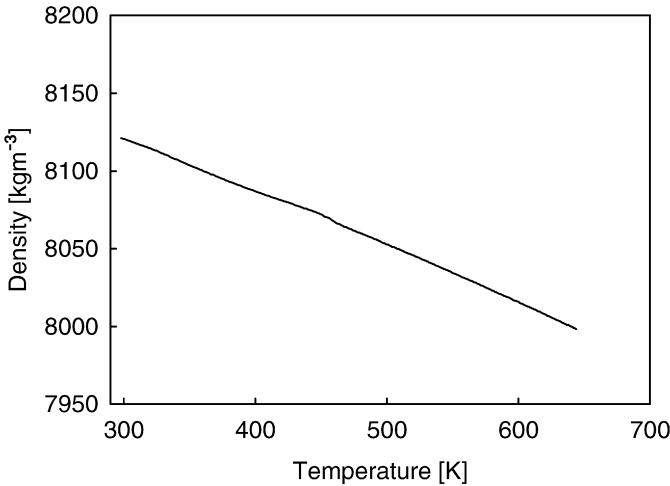


Fig. 4. Temperature dependence of the density.

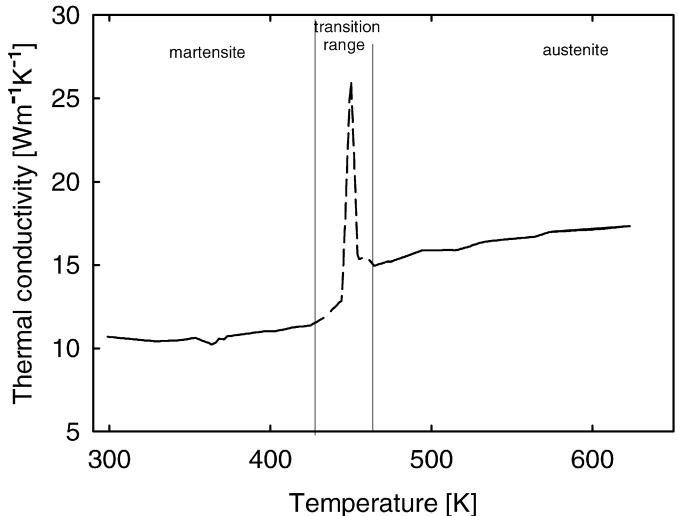


Fig. 6. Temperature dependence of the thermal conductivity.

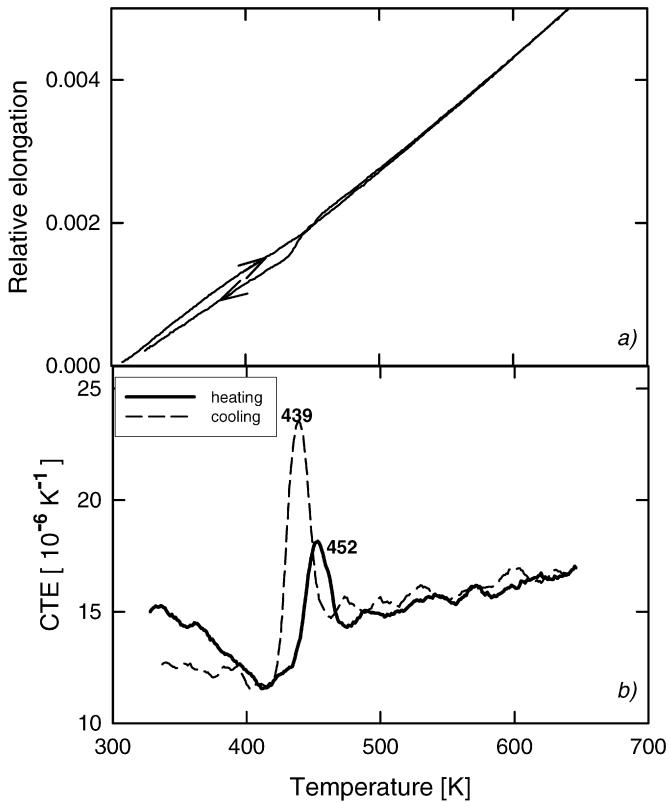


Fig. 5. Temperature dependence of the relative elongation (a) and the CTE (coefficient of thermal expansion) (b).

temperature obtained from the temperature dependence of the thermal diffusivity was 450 K, similar to the value 449 K obtained from the temperature dependence of  $\Delta T_M$ .

Thermal conductivity is determined to be a product of thermal diffusivity, density and specific heat is shown in Fig. 6. The value of the thermal conductivity was determined with accuracy  $\pm 7\%$ . Three temperature regions can be seen the region of the martensite, transient region and austenite region. The austenite has a higher thermal conductivity than the martensite.

A peak appears in the transition region. This is a consequence of the peak of the specific heat. This peak, however,

has no physical meaning as the heat conduction equation (1) was solved with the boundary condition assuming that no phase transformation occurs in the material ( $c_p$ ,  $\rho$  and  $\lambda$  are not dependent on  $T$ ). It was mentioned in the introduction that peaks in the temperature dependence of the thermal conductivity in the transient temperature region were found for various materials. However, these peaks, which were obtained by other experimental methods than the flash method have found specific physical interpretation. For example, in [5] this peak found in Ni<sub>2</sub>MnGa by a direct heat-pulse technique was connected with “the additional heat carried by soft phonons”. The results of our work show that peak of the temperature dependent of the thermal conductivity can also be a consequence of the influence of the latent heat on the measured temperature.

The martensite  $\leftrightarrow$  austenite transformation in shape memory alloys has traditionally been regarded as athermal [18–20]. The athermal transformation appears to be instantaneous for all practical time scales. The amount of transformed material do not depend on time, it only depends on temperature.

The martensite  $\leftrightarrow$  austenite phase transformation is a first-order phase transformation where the transition between both phases is localized in a narrow temperature range. This is also visible from our results shown in Figs. 1 and 2. To study the influence of the phase transformation on the heat conduction, we have measured the maximum temperature rise on the opposite side of the sample at various temperatures and for various energies. The change of the input energy was obtained by a change of the distance of the flash lamp from the sample. The results are shown in Fig. 7.

Practically the same dependences were obtained for all temperatures except for 448 K. The substantial decrease of the temperature rise for higher input energies is unambiguous influence of the phase transformation on the heat flow in the sample after irradiation. Fig. 8 shows the time dependence of the temperature rise for elected temperatures with the input energy corresponding to a flash lamp distance of 190 mm. The region of the quasi-stationary behavior can be found on each curve in Fig. 8.

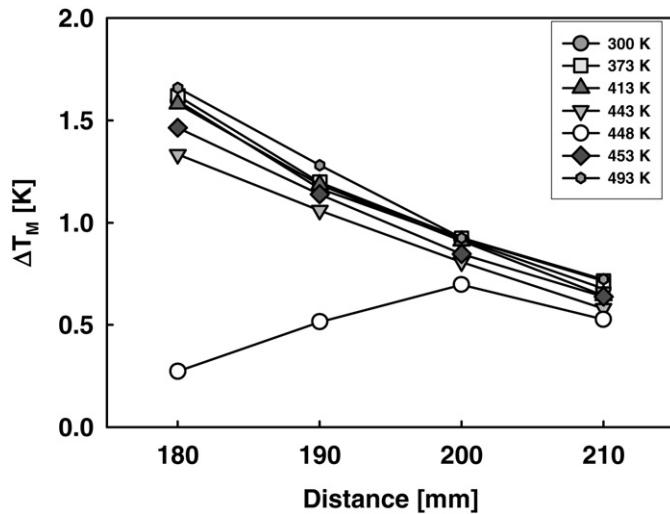


Fig. 7. Dependence of the temperature rise  $\Delta T_M$  on distance of the Xe-flash lamp from the sample.

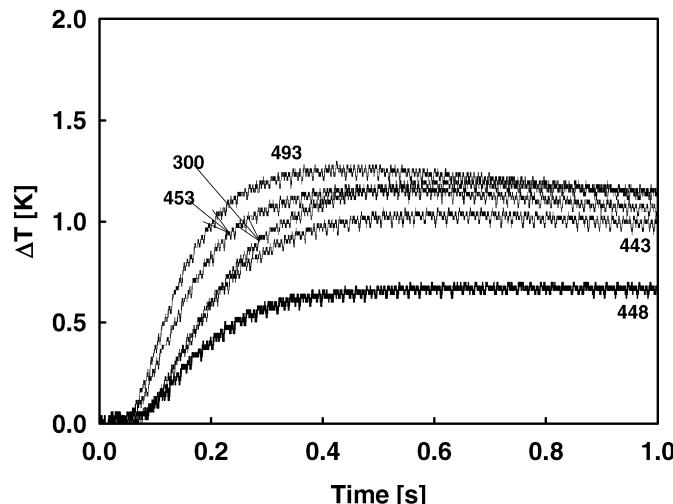


Fig. 8. Time dependence of the temperature rise  $\Delta T$  (distance of the flash lamp from the sample was 190 mm)

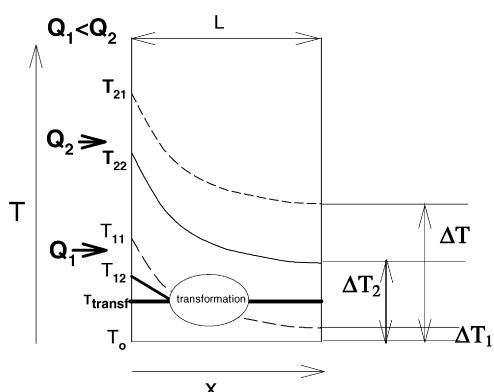


Fig. 9. Scheme of the heat conducting in the sample thickness  $L$  for any time;  $Q_1, Q_2$ —input energy,  $T$  is temperature and  $\Delta T$  is the maximum temperature rise at  $x = L$ .

At this state we have proposed a scheme presented in Fig. 9. It is assumed that the heat flows only in one dimension and that the starting temperature ( $T_0$ ) is close to but below the transient

temperature. At temperature  $T_o$  only martensite exists in the sample. After irradiation the input energy ( $Q_2, Q_1$ ) is absorbed in the sample surface and its temperature rises. If no phase transformation occurred in the material (material would be only martensite) then the temperature would reach  $T_{11}$  or  $T_{21}$ . In this case the temperature in the sample would decrease following the dashes lines indicated in the scheme.

If, however, the surface temperature exceeds  $T_{\text{transf}}$  the phase transformation martensite  $\rightarrow$  austenite occurs (athermal phase transformations depend only on the temperature). The latent heat is consumed (Eq. (3)) and the surface temperature is lower ( $T_{12}$  and  $T_{22}$ ) than in the case without the phase transformation. A part of the input energy is retained in the form of latent heat. The temperature decreases in the sample with time and increasing distance from the surface [13].

When the temperature decreases below  $T_{\text{transf}}$ , the reverse phase transformation austenite  $\rightarrow$  martensite takes place, the latent heat is released and the temperature increases. For the case of lower input energy  $Q_1$  this process occurs inside the sample and the resultant temperatures measured at  $x = L$  does not detect any phase transformation (Fig. 7, distance 200 and 210 mm). The measured temperature rise  $\Delta T_M$  is not influenced by the phase transformation, because the latent heat consumed at the beginning of the transformation process in the sample surface is released inside the sample (in the place where the temperature decreased below  $T_{\text{transf}}$ ).

If the input energy is sufficiently high ( $Q_2$ ) then  $T_{\text{trans}}$  is not reached in the sample and the measured temperature rise at  $x = L$  is lower than for the case without phase transformation ( $\Delta T_2 < \Delta T$ ). The reverse phase transformation occurs in the sample after longer time than the time where  $\Delta T_M$  was determined. Fig. 8 shows that after achieving the maximum value the sample temperature decreases more slowly at 448 K than at other temperatures.

The phase transformation  $\text{martensite} \leftrightarrow \text{austenite}$  and the heat conduction take place in the material together. The  $\text{martensite} \leftrightarrow \text{austenite}$  is the athermal phase transformation, which takes place almost immediately when the transformation temperature is reached. The results show that the thermal conductivity and the thermal diffusivity are very important parameters in determining the temperature inside of the material where the phase transformation takes place. However, these parameters have been largely neglected in all studies of the  $\text{martensite} \leftrightarrow \text{austenite}$  phase transformations.

## 4. Conclusions

The phase transformation martensite  $\rightarrow$  austenite which occurs at  $T \sim 450$  K during heating in  $\text{Ni}_{53.6}\text{Mn}_{27.1}\text{Ga}_{19.3}$  leads to a drop on the temperature dependence of the thermal diffusivity. The thermal diffusivity of the austenite is higher by about 40% than of the martensite. In the temperature range of the phase transformation, the temperature rise after irradiation of the sample sharply decreases due to the absorption in the form of latent heat. This effect can influence the value of the measured temperature in the critical temperature range around the transformation and therefore

affects all physical parameters derived. The thermal conductivity has the same character as the thermal diffusivity. The phase transformation takes place in a narrow temperature range.

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