Anisotropy of the Magnetocaloric Effect in the $Ni_{49.6}Mn_{27.6}Ga_{22.8}$ Single Crystal

R. Wroblewski*, K. Sielicki and M. Leonowicz
Faculty of Material Science and Engineering, Warsaw University of Technology, Wołoska 141, 02-507 Warsaw, Poland

(Received February 2, 2015)

The magnetocaloric effect anisotropy in the $Ni_{49.6}Mn_{27.6}Ga_{22.8}$ single crystal was investigated. In the examined alloy the structural phase transition and magnetic transition occur at room temperature and around 370 K, respectively. The magnetic entropy change, at those two temperatures, was determined on the basis of isothermal and isofield curves, recorded at fields up to 1200 kA/m (1.5 T) with temperature steps of 2.5 and 5 K. Although the calculated values of magnetic entropy change are relatively small, ≈0.7 J/(kg K), an anisotropy of the magnetocaloric effect is observed with a magnetic field applied along the main crystallographic directions of the single crystal. The magnetic entropy change at the structural phase transition depends on the orientation. The weakest magnetocaloric effect occurs when the field is applied along [1 0 0] direction whereas the highest magnetocaloric effect value is reached along [0 0 1] direction, which is an easy magnetization axis. Such behaviour can be explained with the high magnetocrystalline anisotropy of the martensitic phase. The magnetic entropy change value, at the structural phase transition, obtained for the polycrystalline specimen, is close to that for the [0 0 1] single crystal direction.

DOI: 10.12693/APhysPolA.128.54
PACS: 65.40.gd, 75.30.Gw, 75.30.Sg

1. Introduction

Materials with high magnetocaloric effect (MCE) have attracted considerable attention as a refrigerant for magnetic refrigeration, however, there are very few reports on the dependence of this effect on the single crystal orientation. There is a report on the magnetic anisotropy of the Ni–Mn–Ga single crystals [1] but the work was devoted to magnetic-field-induced strain. One of very few works devoted to the anisotropy of MCE is [2], however the studied material, $TbMnO_3$ finds its application at rather low temperature of several K. There is also a research on the anisotropy of the MCE at room temperature in the $NdCo_5$ single crystal [3] reporting the adiabatic temperature change (ΔT_{ad}) varying from −0.15 to +1.15 K, depending on the magnetic field application angle to the c axis. Recently we reported results of our research on the Ni–Mn–Ga single crystal's magnetocaloric properties [4]. The motivation of the present study is to characterize the anisotropy of the MCE in Ni–Mn–Ga single crystal from the basics.

2. Methods

The $Ni_{49.6}Mn_{27.6}Ga_{22.8}$ single crystal was produced by a Bridgman method. The cube with dimensions of $3 \times 3 \times 3$ mm was cut for further studies. The structure and orientation of the single crystal was determined using four-wheel Kuma Diffraction diffractometer with kappa geometry, Cu K_α radiation, at room temperature. The magnetic entropy change (ΔS_M) was calculated from isothermal and isofield curves at fields up to 1200 kA/m, taken with 2.5 or 5 K steps. The magnetization was measured only along the direction of the applied field. The direct measurements of temperature change (ΔT) were taken at field of 1600 kA/m (2 T) using quasi-adiabatic regime. The field was applied along [1 0 0], [0 1 0] and [0 0 1] directions to the crystal in each single experiment.

*corresponding author; e-mail: r.wroblewski@inmat.pw.edu.pl

3. Results

In order to determine the dependence of the magnetocaloric effect on the crystal orientation the magnetic measurements were performed in three directions, perpendicular to the faces of the single crystal. The following crystallographic directions were examined: [1 0 0], [0 1 0], and [0 0 1].

Results of the calculations of the entropy change are based on two equations. First is the Maxwell relation (used for both transitions)

$$\Delta S_M = \int (\partial M/\partial T)\,\mathrm{d}H, \tag{1}$$

where $\partial M/\partial T$ is the derivative of the magnetization with respect to temperature and $\mathrm{d}H$ is the field variation and second is the Clausius–Clapeyron (used for SPT only)

$$\Delta S = \Delta M_{\mathrm{iso}}/(\mathrm{d}T/\mathrm{d}H), \tag{2}$$

where ΔM_{iso} is a difference between the magnetization of the austenitic and martensitic phases and $\mathrm{d}T/\mathrm{d}H$ is a shift in the transformation temperature caused by the field of 800 kA/m (1 T).

According to the calculations obtained using the Maxwell relation one can observe (Fig. 1) that the highest magnetic entropy change, $|\Delta S_M|$, (0.64 J/(kg K) at 1200 kA/m), at structural phase transformation (SPT) temperature, is reached when the magnetic field is applied along the [0 0 1] direction. The increase of the $|\Delta S_M|$ value can be explained on the basis of the magnetocrystalline anisotropy of the single crystal caused by

the tetragonality of the martensitic structure below room temperature. The short c axis is the easy magnetization axis, thus the entropy change, when magnetizing along it, is larger in comparison with the magnetization along the a or b axes. It is noteworthy that [0 0 1] direction in martensite is identical to [0 0 1] direction in austenite [5]. Lower value of $|\Delta S_M|$ (–0.41 J/(kg K) at 1200 kA/m) is reached along the [0 1 0] direction. The smallest entropy change (+0.15 J/(kg K) at 1200 kA/m), at SPT temperature, occurs when the field is applied along the [1 0 0] direction. Additionally, an interesting phenomenon can be observed — the magnetic entropy changes its sign and inverse magnetocaloric effect occurs. The reason for such behaviour is the change of the magnetization rate during the SPT when applying the field along [1 0 0] direction. The field of 800 kA/m, and lower, is too small to saturate the martensite along that axis and the magnetization of the austenite, after the SPT is higher. Similar phenomenon was observed in $Ni_{54.5}FeMn_{20}Ga_{24.5}$ alloy [6].

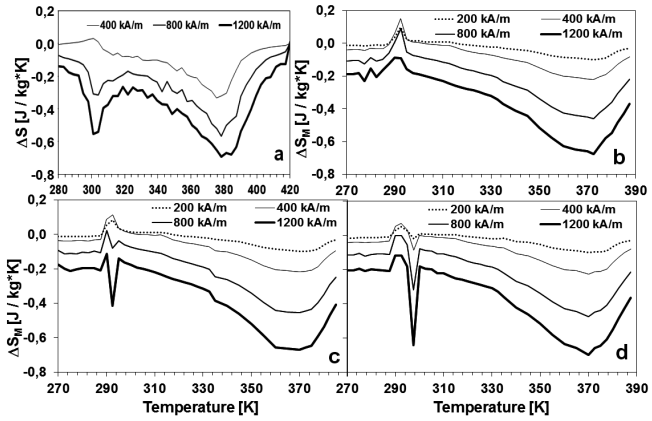

Fig. 1. Field induced magnetic entropy changes in $Ni_{49.6}Mn_{27.6}GA_{22.8}$ poly-crystalline (a) and single-crystalline samples: (b) [1 0 0]; (c) [0 1 0]; (d) [0 0 1].

The values of the magnetic entropy change at the Curie temperature are of the same value in each direction as well as in a polycrystalline sample and are equal to -0.7 J/(kg K). It can be easily explained when one recalls the cubic structure of the austenite which exhibits no magnetocrystalline anisotropy.

TABLE

Field induced magnetic entropy and temperature changes in $Ni_{49.6}Mn_{27.6}Ga_{22.8}$ alloy.

Direction/ sample	ΔS [J/(kg K)] @ H=1200 kA/m			H=1600 kA/m
	Maxwell @ SPT	Maxwell @ T_C	C–C @ SPT	ΔT [K]
[100]	+0.15	– 0.67	– 0.38	0.107
[010]	– 0.41	– 0.67	– 0.4	0.105
[001]	– 0.64	– 0.69	– 0.48	0.109
polycrystalline	– 0.55	– 0.7	– 0.64	0.106

Values of ΔS achieved using Clausius–Clapeyron (C–C) equation (Table) differ slightly from those achieved with the Maxwell relation. This is due to the fact that the SPT is a first-order phase transition and rapid changes in magnetization can lead to spurious effects like spikes on the ΔS vs. T plots resulting from integration of the almost discontinuous curve [7].

The most surprising result is the lack of dependence of ΔT on the direction, however it could be explained by the relatively low and similar values of ΔS which is a result of a small change of magnetization between martensite and austenite.

The dependences of the entropy change on the crystal orientation are similar to those regarding magnetocaloric properties of the $TbMnO_3$ single crystal [2].

4. Conclusion

Concluding, we found that the single crystal $Ni_{49.6}Mn_{27.6}Ga_{22.8}$, having a cubic austenite phase at room temperature, has a structural transition at ≈292 K and Curie point at ≈370 K. The magnetic entropy change depends on the crystal orientation and its absolute value reaches maximum along the [0 0 1] axis irrespective of the equation used for calculations, however obtained values differ slightly. The field induced temperature change seems to be independent of the direction of the applied field.

Acknowledgments

This project is financed by the Polish National Science Centre under the agreement UMO-2011/01/D/ST8/02641.

References

[1] A. Sozinov, A.A. Likhachev, N. Lanska, K. Ullakko, *Appl. Phys. Lett.* **80**, 1746 (2002).

[2] J.L. Jin, X.Q. Zhang, G.K. Li, Z.H. Cheng, L. Zheng, Y. Lu, *Phys. Rev. B* **83**, 184431 (2011).

[3] S.A. Nikitin, K.P. Skokov, Y.S. Koshkid'ko, Y.G. Pastushenkov, T.I. Ivanova, *Phys. Rev. Lett.* **105**, 137205 (2010).

[4] R. Wróblewski, K. Sielicki, W. Maziarz, M. Leonowicz, in: *5th IIF-IIR Conf. on Magnetic Refrigeration at Room Temperature Thermag V, Grenoble (France)*, 2012, p. 199.

[5] A. Planes, L. Mañosa, M. Acet, in: *MRS Fall Meeting, Boston (USA)*, 2007, p. 1.

[6] J.F. Duan, P. Huang, H. Zhang, Y. Long, G. Wu, R. Ye, Y. Chang, F. Wan, *J. Magn. Magn. Mater.* **309**, 96 (2007).

[7] S. Fabbrici, J. Kamarad, Z. Arnold, F. Casoli, A. Paoluzi, F. Bolzoni, R. Cabassi, M. Solzi, G. Porcari, C. Pernechele, F. Albertini, *Acta Mater.* **59**, 412 (2011).