AIP Journal of Applied Physics

Magnetocaloric and thermomagnetic properties of Ni2.18Mn0.82Ga Heusler alloy in high magnetic fields up to 140 kOe

Alexander P. Kamantsev, Victor V. Koledov, Alexey V. Mashirov, Elvina T. Dilmieva, Vladimir G. Shavrov, Jacek Cwik, Anton S. Los, Victor I. Nizhankovskii, Krzysztof Rogacki, Irina S. Tereshina, Yuriy S. Koshkid'ko, Maria V. Lyange, Vladimir V. Khovaylo, and Pnina Ari-Gur

Citation: Journal of Applied Physics **117**, 163903 (2015); doi: 10.1063/1.4918914
View online: http://dx.doi.org/10.1063/1.4918914
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/117/16?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **117**, 163903 (2015)

Magnetocaloric and thermomagnetic properties of $Ni_{2.18}Mn_{0.82}Ga$ Heusler alloy in high magnetic fields up to 140 kOe

Alexander P. Kamantsev,[1,2,a)] Victor V. Koledov,[1,2] Alexey V. Mashirov,[1,2] Elvina T. Dilmieva,[1] Vladimir G. Shavrov,[1] Jacek Cwik,[2] Anton S. Los,[2] Victor I. Nizhankovskii,[2] Krzysztof Rogacki,[2] Irina S. Tereshina,[2,3] Yuriy S. Koshkid'ko,[2,4] Maria V. Lyange,[5] Vladimir V. Khovaylo,[5,6] and Pnina Ari-Gur[7]

[1]*Kotelnikov Institute of Radio-engineering and Electronics of RAS, Moscow 125009, Russia*
[2]*International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw 53-421, Poland*
[3]*Baikov Institute of Metallurgy and Material Science of RAS, Moscow 119991, Russia*
[4]*Faculty of Metallurgy and Materials Engineering, VSB-Technical University of Ostrava, Ostrava-Poruba 708 33, Czech Republic*
[5]*Department of Functional Nanosystems and High-temperature Materials, National University of Science and Technology "MISIS," Moscow 119049, Russia*
[6]*Department of Electrical and Electronic Engineering, ITMO University, St. Petersburg 197101, Russia*
[7]*Department of Mechanical and Aerospace Engineering, Western Michigan University, Kalamazoo, Michigan 49008, USA*

(Received 29 January 2015; accepted 11 April 2015; published online 22 April 2015)

Measurements of the adiabatic temperature change (ΔT) and the specific heat transfer (ΔQ) of $Ni_{2.18}Mn_{0.82}Ga$ Heusler alloy were taken in order to quantify the direct giant magnetocaloric effect of the alloy when it is in the vicinity of magneto-structural phase transition (PT) from paramagnetic austenite to ferromagnetic martensite, and their results are presented. A new vacuum calorimeter was used to simultaneously measure ΔT and ΔQ of magnetocaloric materials with a Bitter coil magnet in fields of up to $H = 140$ kOe. Other thermomagnetic properties of this alloy were investigated using standard differential scanning calorimetry and PPMS equipment. The maximal values of magnetocaloric effect in $H = 140$ kOe were found to be $\Delta T = 8.4$ K at initial temperature 340 K and $\Delta Q = 4900$ J/kg at 343 K. Using this direct method, we show that the alloy indeed demonstrates the largest value of ΔQ as compared with previously published results for direct measurements of magnetocaloric materials, even though at 140 kOe the magnetic field-induced magnetostructural PT is still not complete. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4918914]

I. INTRODUCTION

Giant magnetocaloric effect (GMCE) is observed in some magnetic materials such as $Gd_5(Si_{1-x}Ge_x)$ and Ni_2MnGa in the vicinity of the joint magnetostructural phase transitions (PTs) under sufficiently high external magnetic field. GMCE is very attractive from a fundamental point of view in the study of the interaction between subsystems in a solid state body under conditions of magnetic and structural instability. Investigation of GMCE is of an ever growing practical interest, because it is considered a key phenomenon in the development of a new technology of solid state magnetic refrigerators and heat pumps for wide range of applications.[1] High cooling power of such devices can be achieved only at a high frequency of heat transfer cycles and at large amounts of heat (ΔQ), which can be transferred in one cycle from the cold end to the hot end per unit of mass of the magnetic working body. The maximal frequency depends on the geometry of the working body[2] and the fundamental restrictions on the rate of PT[3] in magnetic material. The transferred heat is expected to be maximal as a result of the additive effect of the magnetic and structural subsystems to the total energy of magnetostructural PT when the two transformation temperatures merge. So far, no reliable information about ΔQ of the most of promising magnetic materials has been available. The indirect data on ΔQ, obtained from calculation of magnetic entropy from isothermal magnetization measurements and heat capacity taken from differential scanning calorimetry (DSC) measurements at zero field, are often contradictory.[4] Recently, there has been a growing trend to develop direct experimental techniques for measurement of ΔQ.[5–9]

In the present work, a new experimental approach was used for the direct measurement of the specific heat transferred ΔQ when changing the magnetic field under quasi-isothermal conditions,[10,11] and apply a new design of the vacuum calorimeter for simultaneous measurements of both adiabatic temperature change ΔT and specific heat transferred ΔQ of magnetic materials, using Bitter coil magnet with fields of up to $H = 140$ kOe. It was suggested that in $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys the thermoelastic martensitic and ferromagnetic PT are coupled (i.e., the order-disorder magnetic transition occurs simultaneously with the order-order crystallographic PT) in the range of compositions $x = 0.18-0.20$, giving rise to GMCE. This makes the alloys attractive for many applications,[12] though the direct measurements of ΔQ and ΔT are still restricted to middle fields (below 20 kOe), not sufficient for complete magnetostructural PT; the reason is that the sensitivity to temperature of

a)E-mail: kama@cplire.ru

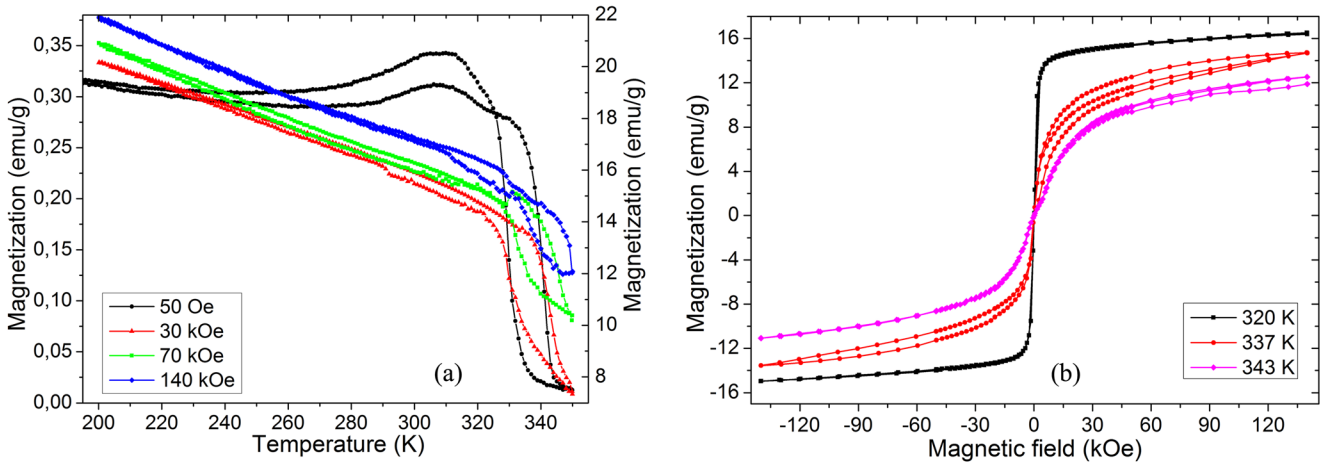

FIG. 1. (a) Magnetization vs. temperature at different fields. The left scale is for the low field (50 Oe), the right scale for the high fields: 30 kOe, 70 kOe, and 140 kOe. (b) Magnetization vs. magnetic field at different temperatures: 320 K, 337 K, and 343 K.

magnetostructural PT in $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys is less than 0.1 K/kOe.[13,14] The insufficient magnetic fields for complete PT lead to an underestimate of the value of GMCE and ambiguous data.[4,8,9] The purpose of the present work was to apply the new direct experimental technique to quantitatively test GMCE in $Ni_{2.18}Mn_{0.82}Ga$ Heusler alloy in the fields of Bitter coil magnet up to 140 kOe.

II. EXPERIMENTAL DETAILS

A polycrystalline $Ni_{2.18}Mn_{0.82}Ga$ ingot was prepared by conventional arc-melting method in argon atmosphere. The ingot was homogenized at 1073 K for 50 h. The structure of this alloy was studied and reported elsewhere.[15] The thermomagnetic measurements were performed on QD PPMS using a AC/DC Measurement System. Magnetization vs. temperature measurements were carried out in the temperature range from 200 K to 350 K with a rate of change of 1 K/min on sweep mode under different magnetic fields: 50 Oe, 30 kOe, 70 kOe, and 140 kOe (Fig. 1(a)). A PT temperature shift of about 0.1 K/kOe was observed under the applied magnetic field. The following protocol (under sweep mode) was used for the magnetization vs. magnetic-field measurements: increasing field up to +140 kOe, then decreasing down to −140 kOe, then increasing up to +140 kOe. The increment of the field was about 100 Oe/s at different temperatures in the vicinity of PT (Fig. 1(b)).

The martensitic PT temperatures and the latent heat during transformation were determined by DSC at heating/cooling rates of 10 K/min. As seen from Fig. 2, DSC scans of the sample demonstrate exothermic and endothermic peaks, which are associated with the martensitic PT. The characteristic transition temperatures $M_s = 331$ K, $M_f = 317$ K and $A_s = 336$ K, $A_f = 351$ K corresponding to the start and finish temperatures of direct and reverse martensitic transformation, respectively, are indicated in Fig. 2. The transition temperatures were determined as a crossing point between the extrapolation lines of the peaks and the base line. Calculated from the DSC data, the heat exchanged upon direct ($L_{H\to L}$) and reverse ($L_{L\to H}$) PT are $L_{H\to L} = +6500$ J/kg and $L_{L\to H} = -6180$ J/kg. These values of latent heat are smaller than $L = 9600$ J/kg obtained on a sample with the same composition $Ni_{2.18}Mn_{0.82}Ga$.[15] Big values of latent heat result from heat treatment. The sample reported in Ref. 15 was homogenized at 1050 K for 9 days, and quenched in ice water. The average of the absolute values of $|L_{H\to L}|$ and $|L_{L\to H}|$ was taken as the change of enthalpy ΔE. In the case of thermoelastic martensitic transformation, the configuration contributions to the entropy change are absent. This makes it possible to estimate the total entropy change at the martensitic transformation as $\Delta S_{DSC} = \Delta E/T_m$, where $T_m = (M_s + A_f)/2$ is the thermodynamic equilibrium temperature.[15] For the experimentally determined values of $\Delta E = 6340$ J/kg and $T_m = 341$ K, the entropy change is equal to $\Delta S_{DSC} = 18.6$ J/kg K.

The experimental vacuum calorimeter was developed to simultaneously measure ΔT and ΔQ magnetocaloric effect under high magnetic fields. Two samples are placed into the calorimeter in order to obtain in one experiment both ΔT and ΔQ. The first sample was bulk "sample_1" (for ΔT) and a smaller plate "sample_2" (for ΔQ), see Fig. 3(a). Sample_1 ($m_1 = 4.299$ g) was placed into the vacuum chamber at adiabatic conditions. Sample_2 ($m_2 = 0.495$ g) was glued (by heat-conducting glue) on a massive tungsten block ($M_b = 10.866$ g)

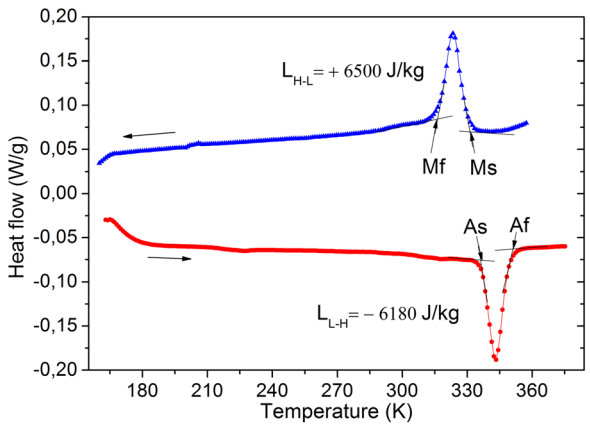

FIG. 2. Differential scanning calorimetry scans of $Ni_{2.18}Mn_{0.82}Ga$. M_s, M_f and A_s, A_f denote start and finish temperatures of the direct and reverse martensitic PT, respectively.

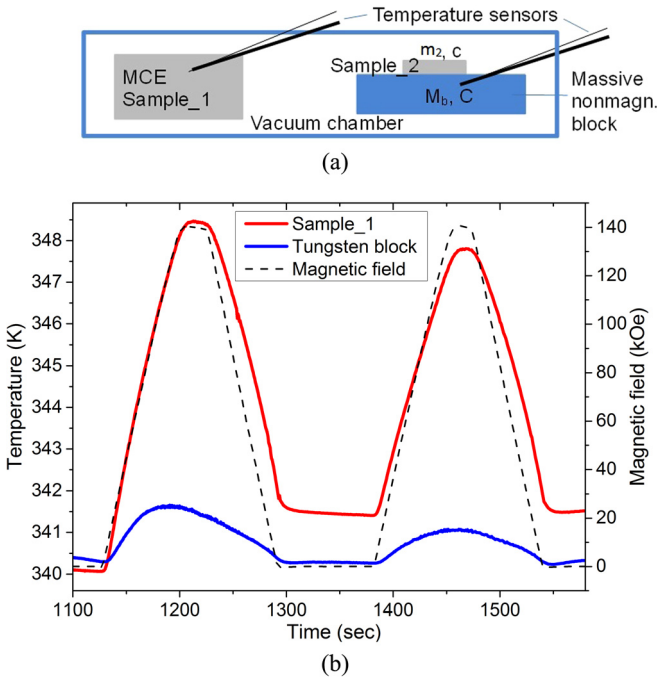

FIG. 3. (a) The scheme of the experimental setup for simultaneous measurements of ΔT and ΔQ in Bitter coil magnet. (b) The time dependence of the magnetic field (H) change and the corresponding adiabatic temperature change (ΔT) of sample_1 and the temperature change of the tungsten block (ΔT_b) connected to sample_2.

to maintain quasi-isothermal conditions and was placed into the same vacuum chamber. The experimental estimate of the heat transferred ΔQ from the sample to the block in quasi-isothermal conditions was accomplished by measuring ΔT_b—the temperature change of the block when the magnetic field is changed.[10,11] ΔQ can be calculated as

$$\Delta Q \approx (M_b/m_2) \times C \times \Delta T_b, \quad (1)$$

where C is the specific heat of the block and $M_b \gg m_2$. The temperatures of sample_1 and the tungsten block were measured with the help of platinum thermoresistors PT 1000 under constant current.

The protocol of the experiment was as follows. The vacuum calorimeter was placed into a Bitter coil magnet. The vacuum in the chamber was achieved by a forepump (down to pressure 0.4 Pa). The initial temperature was set with the help of thermo-control system to equilibrium. Then, the magnetic field was turned on at a constant rate of 2.0 kOe/s up to 140 kOe then turned off at the same rate (Fig. 3(b)). The magnitude of magnetic field was measured by a Hall probe. Corresponding temperature changes of sample_1 and the tungsten block are shown in Fig. 3(b). Summary data of ΔT and ΔQ measurements for the $Ni_{2.18}Mn_{0.82}Ga$ alloy in H = 140 kOe are presented in Figs. 4(a) and 4(b), respectively. A big difference of the ΔT and ΔQ values between the 1st and the 2nd cycles of magnetic field application was observed when the initial temperature is between M_f and A_f. It is connected with residuals of martensitic phase after the 1st removal of magnetic field. The initial temperature must be more than A_f in order to avoid such effect in cycle of magnetic refrigeration based.

III. RESULTS AND DISCUSSION

It is important to note that although Heusler alloys of Ni_2MnGa system have been at the center of attention for almost two decades, thanks to their magnetic-field controlled martensitic transition governing GMCE and shape memory effect, no data on direct measurement of MCE have been published attributed to complete magnetostructural PT by magnetic field.[13–19] We demonstrate by the direct method that even though a magnetic field, as strong as H = 140 kOe, does not lead to complete PT from paramagnetic austenite to ferromagnetic martensite, the maximal value of heat transferred ΔQ = 4900 J/kg obtained at 343 K in this field (Fig. 4(b)) exceeds the highest values reported in previously published works. The fact that the maximal value ΔQ = 4900 J/kg is less than the latent heat of the alloy $L_{H\to L}$ = 6500 J/kg obtained by DSC in zero magnetic field can be explained by the incomplete magnetostructural PT. Following the magnetization data in Fig. 1(a), we can say,

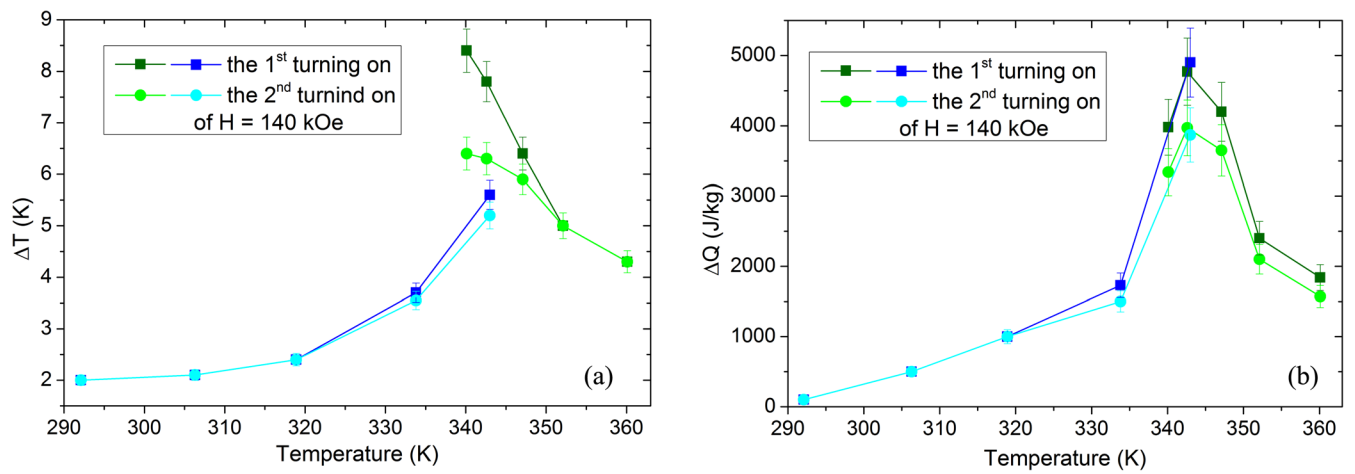

FIG. 4. The results of direct ΔT (a) and ΔQ (b) measurements on the $Ni_{2.18}Mn_{0.82}Ga$ sample. Square points are the 1st and circle points are the 2nd consecutive run of turning on a magnetic field of H = 140 kOe at the same temperature. Dark- and light-blue points are series of experiments with progressive heating. Dark- and light-green points are series of experiments with preliminary heating up to 370 K and sequential cooling down to the required temperature for the measurements.

that shift of T_m in H = 140 kOe is not big—about 10 K. We apparently need to apply more magnetic fields for inducing complete PT. Incomplete PT can also be responsible for the observation that direct ΔT measurement shows big irreversibility of magnetostructural PT: the maximal value is ΔT = 8.4 K when first turning on the magnetic field, but the second time gives a value of 2 K smaller at initial temperature 340 K (Fig. 4(a)). Even so, the maximal ΔT and ΔQ values obtained in the present work are recorded high among other Heusler alloys. Moreover, ΔQ measured in the present work exceeds any results previously obtained by direct measurements in any other magnetic materials.[5–9] In this sense, the MCE near the magnetostructural PT in $Ni_{2.18}Mn_{0.82}Ga$ alloy deserves the name "giant." Recent direct data of ΔT and ΔQ for Gd up to 140 kOe are presented in Ref. 20. These data may compete with GMCE in Heusler alloy. Apparently, the maximal ΔT = 8.4 K for $Ni_{2.18}Mn_{0.82}Ga$ is less than ΔT = 17.7 K for Gd.[20] This may be due to the fact that the effective heat capacity of the alloy with magnetostructural PT strongly exceeds the heat capacity for Gd.

It may be concluded that further studies are needed to insure complete magnetostructural PT in order to reveal the full potential of Ni_2MnGa Heusler alloys as promising magnetocaloric working body for room temperature refrigeration. In general, the direct measurement of ΔQ and ΔT using the new technique under sufficiently high magnetic fields will be an important contribution to the knowledge of MCE in a wide variety of magnetic materials being developed by research groups around the world.

ACKNOWLEDGMENTS

The work was supported by Russian Science Foundation Grant No. 14-22-00279.

[1]K. A. Gschneidner, Jr. and V. K. Pecharsky, Int. J. Refrig. **31**, 945 (2008).
[2]A. Šarlah, J. Tušek, A. Poredošet, and S. Vestnik, J. Mech. Eng. **58**, 16 (2012).
[3]A. P. Kamantsev, V. V. Koledov, V. G. Shavrov, and I. S. Tereshina, Solid State Phenom. **215**, 113 (2014).
[4]V. Khovaylo, J. Alloys Compd. **577S**, S362 (2013).
[5]T. Plackowski, Yu. Wang, and A. Junod, Rev. Sci. Instrum. **73**, 2755 (2002).
[6]V. Basso, M. Küpferling, C. P. Sasso, and L. Giudici, Rev. Sci. Instrum. **79**, 063907 (2008).
[7]J. Kamarád, J. Kaštil, and Z. Arnold, Rev. Sci. Instrum. **83**, 083902 (2012).
[8]E. Stern-Taulats, P. O. Castillo-Villa, L. Mañosa, C. Frontera, S. Pramanick, S. Majumdar, and A. Planes, J. Appl. Phys. **115**, 173907 (2014).
[9]G. Porcari, F. Cugini, S. Fabbrici, C. Pernechele, F. Albertini, M. Buzzi, M. Mangia, and M. Solzi, Phys. Rev. B **86**, 104432 (2012).
[10]A. Kamantsev, V. Koledov, E. Dilmieva, A. Mashirov, V. Shavrov, J. Cwik, I. Tereshina, V. Khovaylo, M. Lyange, L. Gonzalez-Legarreta, B. Hernando, and P. Ari-Gur, EPJ Web Conf. **75**, 04008 (2014).
[11]A. P. Kamantsev, V. V. Koledov, A. V. Mashirov, E. T. Dilmieva, V. G. Shavrov, J. Cwik, and I. S. Tereshina, Bull. Russ. Acad. Sci. Phys. **78**(9), 936 (2014).
[12]E. Kalimullina, A. Kamantsev, V. Koledov, V. Shavrov, V. Nizhankovskii, A. Irzhak, F. Albertini, S. Fabbrici, P. Ranzieri, and P. Ari-Gur, Phys. Status Solidi C **11**, 1023 (2014).
[13]A. A. Cherechukin, I. E. Dikshtein, D. I. Ermakov, A. V. Glebov, V. V. Koledov, D. A. Kosolapov, V. G. Shavrov, A. A. Tulaikova, E. P. Krasnoperov, and T. Takagi, Phys. Lett. A **291**, 175 (2001).
[14]A. N. Vasil'ev, A. D. Bozhko, V. V. Khovailo, I. E. Dikshtein, V. G. Shavrov, V. D. Buchelnikov, M. Matsumoto, S. Suzuki, T. Takagi, and J. Tani, Phys. Rev. B **59**, 1113 (1999).
[15]V. V. Khovailo, T. Takagi, J. Tani, R. Z. Levitin, A. A. Cherechukin, M. Matsumoto, and R. Note, Phys. Rev. B **65**, 092410 (2002).
[16]V. D. Buchelnikov, S. V. Taskaev, A. M. Aliev, A. B. Batdalov, A. M. Gamzatov, A. V. Korolyov, N. I. Kourov, V. G. Pushin, V. V. Koledov, V. V. Khovailo, V. G. Shavrov, and R. M. Grechishkin, Int. J. Appl. Electron. Mech. **23**, 65 (2006), available at http://iospress.metapress.com/content/fdv7yxjg64m83jqy/.
[17]V. V. Khovaylo, K. P. Skokov, Yu. S. Koshkid'ko, T. Takagi, and A. N. Vasiliev, Phys. Rev. B **78**, 060403 (2008).
[18]A. Aliev, A. Batdalov, S. Bosko, V. Buchelnikov, I. Dikshtein, V. Khovailo, V. Koledov, R. Levitin, V. Shavrov, and T. Takagi, J. Magn. Magn. Mater. **272–276**, 2040 (2004).
[19]I. E. Dikshtein, D. I. Ermakov, V. V. Koledov, A. A. Cherechukin, and V. G. Shavrov, JETP Lett. **72**, 373 (2000).
[20]A. P. Kamantsev, V. V. Koledov, A. V. Mashirov, E. T. Dilmieva, V. G. Shavrov, J. Cwik, and I. S. Tereshina, Solid State Phenom. **233–234**, 216 (2015).