Hydrostatic pressure-tuned magnetostructural transition and magnetocaloric effect in Mn-Co-Ge-In compounds

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Polycrystalline $MnCoGe_{0.99}In_{0.01}$ with magnetostructural transition temperature (T_{mstr}) around 330 K has been prepared by arc-melting technique, and the pressure-tuned magnetostructural transition as well as the magnetocaloric effect (MCE) has been investigated. The experimental results indicate that a pressure (P) smaller than 0.53 GPa can shift T_{mstr} to lower temperature at a considerable rate of 119 K/GPa with the coupled nature of magnetostructural transition unchanged. However, as P reaches 0.53 GPa, the martensitic structural transition temperature (T_M) further shifts to 254 K while the magnetic transition temperature of austenitic phase ($T_C{}^A$) occurs at around 282 K, denoting the decoupling of magnetostructural transition. Further increasing P to 0.87 GPa leads the further shift of T_M to a lower temperature while the $T_C{}^A$ keeps nearly unchanged. Therefore, the entropy change (ΔS) of the $MnCoGe_{0.99}In_{0.01}$ under different magnetic fields can be tailored by adjusting the hydrostatic pressure. https://doi.org/10.1063/1.5006688

INTRODUCTION

MnCoGe-based materials with Ni_2In-type hexagonal structure[1–7] show large magnetocaloric effect (MCE),[1] barocaloric effect (BCE)[2] and giant negative thermal expansion (NTE)[3] behavior. These multifunctional properties warrant people's interest for this kind of materials due to the potential application in solid state refrigeration technique, as well as high-precision pressure-sensitive sensors and devices. The martensitic phase transition (T_M) from the Ni_2In-type hexagonal structure (space group $P6_3/mmc$) to the TiNiSi-type orthorhombic structure (space group Pnma) is supposed to be responsible for these fascinating properties.[4]

Stoichiometric MnCoGe alloy shows ferromagnetic properties with Curie temperature at about 345 K.[5] In the paramagnetic region, a martensitic structural transition from high temperature Ni_2In-type hexagonal to low temperature TiNiSi-type orthorhombic structure takes place at about 420 K with a -3.9% negative volume change.[5,8] It has been also revealed that its intrinsic Curie temperature of hexagonal phase locates at about 283 K.[9,10] More attractively, the magnetic interactions and the structural transition can be adjusted by either chemical pressure, i.e. substitutions,[6] dopings,[7] and interstitial elements[7] or physical pressure.[1,11] Coincidence of magnetic and structural phase transitions has been realized in the composition $MnCoGe_{0.99}In_{0.01}$ through replacing a few Ge by In atoms.[2] Hydrostatic pressure is also an effective way to influence the structural and magnetic properties.[12–14] Early studies by Niziol et al[11] showed that the separated magnetic and structural transitions can be made to be coincident during a range of pressure. Here, we report the influence of hydrostatic pressure

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on the T_{mstr} and MCE for this alloy. A series of pressure (P) including ambient pressure (namely 0 GPa), 0.24 GPa, 0.53 GPa, and 0.87 GPa were selected to study the pressure effect. Under 0 GPa, the $MnCoGe_{0.99}In_{0.01}$ alloy shows a considerable large entropy change ΔS ~ -17.9 $Jkg^{-1}K^{-1}$ for a field change of 5 T around its T_{mstr}~330 K. We found that the application of a pressure smaller than 0.53 GPa can significantly shifts T_{mstr} to lower temperature at a considerable rate of 119 K/GPa. As the pressure reaches 0.53 GPa, T_M is further pushed to 254 K while $T_C{}^A$ is still at a much higher temperature about 282 K, demonstrating the decoupling of magnetic and structural transition.

EXPERIMENTAL DETAILS

The alloy with nominal composition $MnCoGe_{0.99}In_{0.01}$ was prepared by arc-melting technique under Ar atmosphere atmosphere (99.996%) with a base vacuum of 10^{-4}Pa. To make the ingots homogeneous, each one was re-melted for three times. The commercial purities of Mn, Co, Ge, In are 99.9 wt%, 99.9 wt%, 99.999 wt%, and 99.99 wt%, respectively. 1wt% extra Mn was added during sample synthesis to compensate Mn loss. The obtained ingots were wrapped with Mo foil and subsequently homogenized in a sealed quartz tube under vacuum of 10^{-4} Pa at 875 °C for 6 days, then cooled down to room temperature in the furnace. Magnetic properties were measured in superconducting quantum interferometer device (SQUID, MPMS-7 T). Hydrostatic pressure was applied by using a Be-Cu pressure cell, where Daphne 7373 was used as the pressure transferring medium. The pressure inside the cell was calibrated by the shifts of the superconductive transition temperature of Pb. Magnetic entropy change ΔS was calculated based on the magnetization data using Maxwell relation.

RESULTS AND DISCUSSION

Temperature dependence of magnetization (M-T curve) under a magnetic field of 100 Oe for zero-field-cooling (ZFC) and field-cooling (FC) is shown in figure 1(a). The thermal hysteresis between heating and cooling cycles indicates the first-order nature of the transition. $MnCoGe_{0.99}In_{0.01}$ shows the T_{mstr} at ~330 K, defined as the peak position of dM/dT on heating, under 0 GPa and a thermal hysteresis about ~12 K. Upon application of hydrostatic pressure, T_{mstr} shifts to lower temperatures at a rate of ~119 K/GPa with the coupled nature of magnetostructural transition unchanged as the pressure is below 0.53 GPa. From figure 1(a), one can notice that the gap of thermal hysteresis (~12 K) keeps nearly unchanged under a pressure of 0.24 GPa compared to 0 GPa while the T_{mstr} locates at around 285 K.

When the pressure reaches 0.53 GPa, the structural and magnetic transitions become separated. The martensitic transition occurs at round T_M ~ 254 K while magnetic transition of austenitic phase at round $T_c{}^A$ ~ 282 K, as shown in figure 1(a). Further increasing the pressure to 0.87 GPa leads to the further lower T_M at ~226 K while the $T_c{}^A$ keeps nearly unchanged. For the MM`X (where M, M` are 3d transition metals and X is Si or Ge) compounds, the austenitic phase has a smaller unit cell volume than the martensitic phase, indicating that the substitution with smaller atoms or vacancies may shift T_M to a lower temperature by stabilizing hexagonal phases. Indeed, chemical pressure induced magnetostructural transition has been reported in $MnCo_{1-x}Ge$,[15] $Mn_{1-x}CoGe$,[16] and $Mn_{1-x}Cr_xCoGe$.[6] Besides, valence electron concentration (e/a) also plays an important role in lowering T_M and creating magnetostructural transition.[2] Recently, doping larger atoms with fewer valance electrons has been studied in $Mn_{1-x}Al_xCoGe$[17] and $MnCo_{1-x}Zr_xGe$.[18] It was found that the replacement of Mn by Al makes the martensitic transformation temperature decrease, as a result, a first-order magnetostructural transition occurs at $0 \leq x \leq 0.01$ (For x = 0, the Mn loss during the melting is supposed to be responsible for the coupling of the structural and magnetic transitions.). For $0.01 < x \leq 0.02$, T_M is below T_C and the magnetic and structural transitions become separated. For $MnCo_{1-x}Zr_xGe$, the coincidence of structural and magnetic transitions has been observed at x = 0.02. Our previous studies have demonstrated that the substitution of Ge for In can also shift the T_M to lower temperatures in $MnCoGe_{1-x}In_x$, resulting in the magnetostructural coupling at $0 < x < 0.03$.[2] At x = 0.01, the T_{mstr} appears at 330 K for $MnCoGe_{0.99}In_{0.01}$. Hydrostatic pressure has a similar effect with chemical

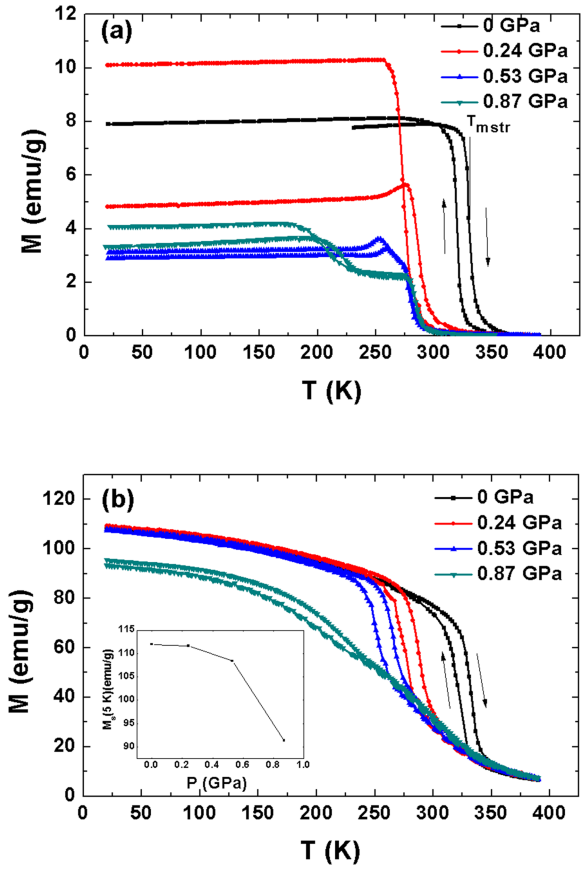

FIG. 1. Temperature dependence of magnetization (*M-T* curve) for $MnCoGe_{0.99}In_{0.01}$ measured using ZFC-FC modes under a magnetic field of 100 Oe (a), and the *M-T* curve at a 5T (b) magnetic field on warming and cooling. Inset: saturation magnetization at 5 K M_s(5 K) vs Pressure.

pressure in reducing volume and stabilizing the hexagonal phase, thus bringing the T_M down to low temperature.[12] Neutron diffraction investigation revealed that the Mn-Mn interlayer distance can be rapidly shortened and the covalent banding between Mn-Mn atoms is strengthened upon an application of hydrostatic pressure, hence leading to the stabilization of the austenitic phase and the shift of T_{mstr} to low temperature.[2]

Figure 1(b) displays the temperature dependent magnetization (*M-T* curve) measured on heating and cooling at a high magnetic field of 5 T under different pressures. One can notice the impact of magnetic field on the magnetization and magnetostructural transition under pressure. The phase transition becomes less sharp, while the gap of thermal hysteresis remains nearly the same, ~12 K, for the all cases of 0 GPa, 0.24 GPa, and 0.53 GPa. The change of magnetization (ΔM) across the transition also shows a difference, which is 53.4, 44.7, 36.1 emu/g for 0 GPa, 0.24 GPa and 0.53 GPa respectively, predicting possible decrease of entropy change with pressure. For P = 0.53 GPa, two distinct transitions T_M and $T_C{}^A$ can be seen from the M-T curves at 0.01 T (figure. 1(a)), which still can be identified at 5T when the logarithmic coordinate is applied for the vertical axis (not shown). It means that the application of 5 T magnetic field does not lead to the magnetostructural coupling. For *P*=0.87 GPa, the transition is significantly broadened due to the decoupling of magnetic and structural transition. An interesting feature is that the saturated magnetization at 5 K keeps the nearly same for the cases of 0 GPa, 0.24 GPa and 0.53 GPa. However, the saturated magnetization at 5 K (M_s(5 K)) under 0.87 GPa largely decreases (see the inset of figure 1(b)). The reason can be ascribed to the change of ferromagnetic coupling between Mn atoms under pressure noting the magnetic moment of the alloy is totally dominated by Mn atoms.[9] Early studies about the effect of hydrostatic pressure on the saturation magnetization of Mn-riched $Ni_{50-x}Mn_{25+x+y}Ga_{25-y}$ showed that physical pressure

can lead to a decrease of saturation magnetization.[19] Detailed studies concluded that the magnetic coupling between Mn atoms is not affected by atomic distance simply, the atomic arrangement and ordering also play an important role. Although no enough structural information can be available for the effect of a high pressure on the atomic occupation in the martensitic orthorhombic phase for present $MnCoGe_{0.99}In_{0.01}$, a critical change of local environments particularly for the Mn-Mn pairs and their surroundings induced by a high pressure should play a dominated role for the observed large decrease of saturation magnetization under 0.87 GPa.

Figure 2 shows the field dependence of magnetization (*M-H* curves) measured up to 5 T at different temperatures under different pressures. Large magnetic hysteresis at temperatures around the T_{mstr} can be observed at 0 GPa, which indicates a field-induced metamagnetic transition from the paramagnetic austenstic phase to the ferromagnetic martensitic phase. However, as the pressure increases, the hysteresis gradually disappeared. For P=0.87 GPa, no clear magnetic hysteresis can be identified. The intrinsic hysteresis is expected to be connected with the electronic band structure and the nucleation during the transition.[20] The process of metamagnetic transition in $LaFe_{11.7}Si_{1.7}$ has been interpreted in terms of activation model.[20] For radii smaller than the critical size of the nucleation, the large surface energy forces new phase bubble to disappear. The application of pressure may influence the atomic distance and hence alters the covalent banding and electronic band structure. As a result, the nucleation during the phase transition may become harder, leading to the gradual disappearance of magnetic hysteresis with pressure. Besides, the frictions from domain rearrangements during the transition also contribute to the hysteresis loss. An application of pressure may significantly influence the microstructure, and the distribution of residual stress and domains have been changed under pressure, which should also play a role to the change of magnetic hysteresis with pressure.

Magnetic hysteresis, which is a sign of field-induced metamagnetic transition, is further studied for P=0 GPa. We measured the M-T curves using SQUID-VSM in the absence of pressure under different magnetic fields of 0.5 T, 1 T, 2 T, and 5 T, as shown in figure 3. Similar magnetic hysteresis appears at temperatures around the T_{mstr}. From figure 3(a), one may notice that the T_{mstr} shifts to higher temperatures with increasing magnetic field. The normalized *M-T* curves are shown in figure 3(b). T_{mstr} is defined as the temperature corresponds to the peak position of *dM/dT* on heating. One can notice that the T_{mstr} shifts to higher temperature at a rate of 1.34 K/T, similar to the driving rate by

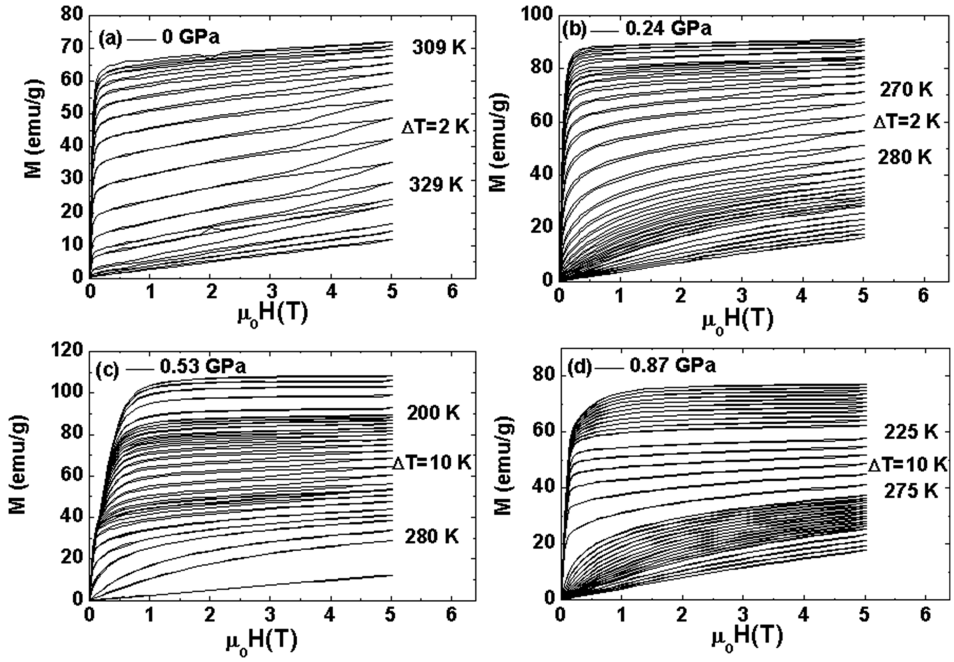

FIG. 2. Isothermal *M-H* curves measured at different temperatures for 0 GPa(a), 0.24 GPa(b), 0.53 GPa(c) and 0.87 GPa(d).

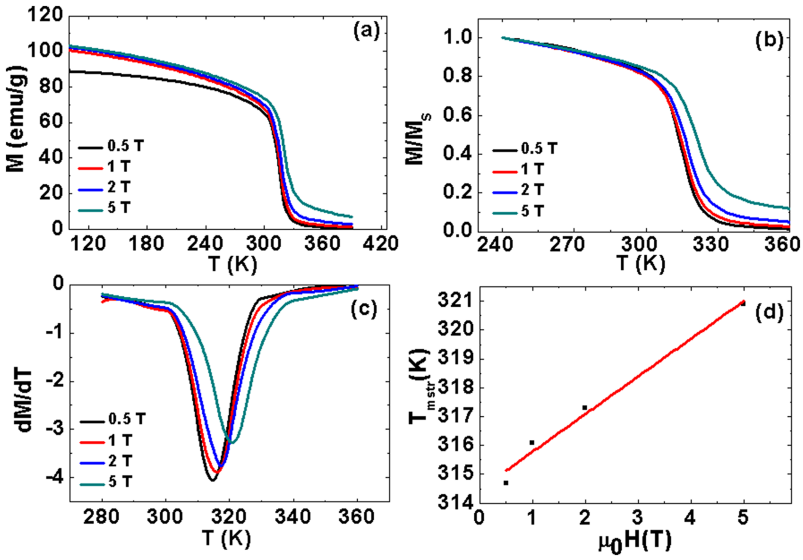

FIG. 3. (a) Temperature dependence of magnetization (*M-T* curve) on heating for 0 GPa under magnetic fields of 0.5 T, 1 T, 2 T and 5 T, (b) Normalized *M-T* curves on heating, (c) *dM/dT* curves at round the T_{mstr}, (d) The dependence T_{mstr} on magnetic field.

magnetic field in the reported MnCrCoGe.[1] However, when comparing figure 1(a) and (b), we found that the 5 T magnetic field shifts the T_{mstr} from 329 K to 333 K at a rate about 0.8 K/T at 0 pressure. This deviation of the shift rate might be relative to the possible difference from sample to sample though all of them were from the same ingot. One knows that the magnetostructural transition is critically dependent on the composition, and the microstructure also plays a key role on the process of magnetostructural transition. The as-prepared MnCoGeIn sample is quite brittle and even naturally cracked into powders. It is quite possible that the microstructure has some difference from powder to powder.

Finally, we turn our attention to the magnetocaloric effect of $MnCoGe_{0.99}In_{0.01}$. Magnetic entropy change ΔS was calculated using Maxwell relation.[21] As shown in figure 4, the maximum of $|\Delta S|$ is 17.9, 15.9, and 10.4 $Jkg^{-1}K^{-1}$ for a magnetic field change (ΔH) of 0-5 T under pressure of 0 GPa, 0.24 GPa and 0.53 GPa respectively. Although the $|\Delta S|$ value decreases with increasing pressure, the width of ΔS peak is broadened covering room temperature. For P=0.53, 0.87 GPa, a clear split appears in the ΔS peak due to the decoupling of structural and magnetic transitions, and the ΔS

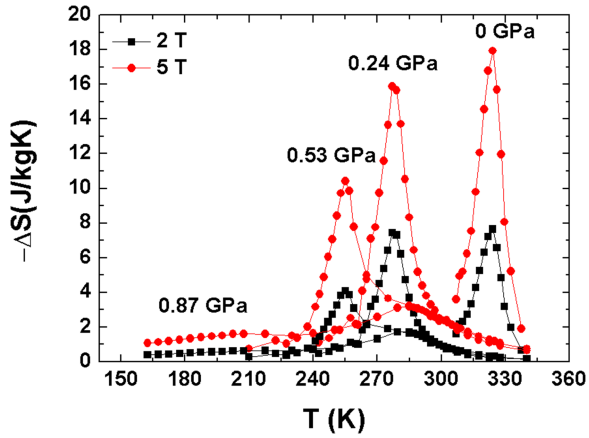

FIG. 4. Temperature dependence of entropy change of $MnCoGe_{0.99}In_{0.01}$ for the magnetic field changes of 0-2 T and 0-5 T under different pressures.

sharply decreases for the case of P=0.87 GPa due to the notable reduction of saturated magnetization (figure 1(b) and its inset). These results suggest that an application of hydrostatic pressure smaller than 0.87 GPa is an effective way in tuning the magnetocaloric effect for present $MnCoGe_{0.99}In_{0.01}$ alloy. Additionally, refrigeration capacity (RC) is another important parameter that can estimate the usefulness of a material as a magnetic refrigerant. It is defined as $RC = -\int_{T_1}^{T_2} \Delta S\,(T)\,dT$, where T_1 and T_2 correspond the temperatures at half width of ΔS peak. The calculated RC is about 203, 200 and 157 Jkg^{-1} under ΔH= 0-5 T for the samples under 0 GPa, 0.24 GPa and 0.53 GPa respectively. However, hysteresis loss injures the performance of RC. People usually use the effective refrigeration capacity (RC_{eff}) with the deduction of maximal hysteresis loss to effectively evaluate the materials. The evaluated RC_{eff} is about 185, 178 and 169 J/kg at 5 T for 0 GPa, 0.24 GPa and 0.53 GPa, respectively. Moreover, one can also notice that the peak position of ΔS can be continuously tunable from 330 K down to 250 K covering room temperature with pressure, which is particularly meaningful for the hybrid field driven refrigeration applications around room temperature.

CONCLUSION

In summary, the pressure effect on magnetostructural transition and magnetocaloric effect has been studied for the polycrystalline $MnCoGe_{0.99}In_{0.01}$ alloys. Our results indicate that the magnetostructural transition shifts to lower temperatures with increasing pressure. Although the ΔS decreases as the pressure is smaller than 0.87 GPa, the effective refrigeration capacity RC_{eff} stays almost unchanged due to the reduction of hysteresis loss with pressure. As the pressure is increased to 0.53, 0.87 GPa, the ΔS peak splits due to the decoupling of the structural and magnetic transition and the ΔS value sharply decreases because of the notable reduction of saturated magnetization. The tunable ΔS and RC_{eff} by pressure is of particular significance for developing the hybrid field driven refrigeration applications.

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[1] L. Caron, N. T. Trung, and E. Bruck, Phys. Rev. B **84**, 020414(R) (2011).
[2] R. R. Wu, L. F. Bao, F. X. Hu *et al.*, Sci. Rep **5**, 18027 (2015).
[3] Y. Y. Zhao, F. X. Fu, L. F. Bao *et al.*, J. Am. Chem. Soc. **137**, 1746–1749 (2015).
[4] W. Jeitschko, Acta Cryst. B **31**, 1187 (1975).
[5] S. Niziol, A. Weselucha, W. Bazela, and A. Szytula, Solid State Commun. **39**, 1081–1085 (1981).
[6] N. T. Trung, V. Biharie, L. Zhang, L. Caron, K. H. J. Buschow, and E. Bruck, Appl. Phys. Lett. **96**, 162507 (2010).
[7] N. T. Trung, L. Zhang, L. Caron, K. H. J. Buschow, and E. Bruck, Appl. Phys. Lett. **96**, 172504 (2010).
[8] T. Kanomata, H. Ishigaki, T. Suzuki, H. Yoshida, S. Abe, and T. Kaneko, J. Magn. Magn. Mater. **140–144**, 131 (1995).
[9] S. Kaprzyk and S. Niziol, J. Magn. Magn. Mater. **87**, 267 (1990).
[10] S. Lin, O. Tegus, E. Bruck, W. Dagula, T. J. Gortenmulder, and K. H. Buschow, IEEE Trans. Magn. **42**, 3776 (2006).
[11] S. Niziol, A. Zieba, R. Zach, M. Baj, and L. Dmowski, J. Magn. Magn. Mater. **38**, 205 (1983).
[12] J. Lyubina, K. Nenkov, L. Schultz, and O. Gutfleisch, Phys. Rev. Lett. **101**, 177203 (2008).
[13] E. Bruck, J. Kamarad, V. Sechovsky, Z. Arnold, O. Tegus, and F. R. de Boer, J. Magn. Magn. Mater. **310**, e1008 (2007).
[14] Y. Tseng, D. Haskel, J. C. Lang, Ya. Mudryk, V. K. Pecharsky, and K. A. Gschneidner, Jr., J. Appl. Phys. **103**, 07B301 (2008).
[15] J. T. Wang, D. S. Wang, C. F. Chen, O. Nashima, T. Kanomata, H. Mizuseki, and Y. Kawazoe, Appl. Phys. Lett. **89**, 262504–262506 (2006).
[16] E. K. Liu, W. Zhu, L. Feng, J. L. Chen, W. H. Wang, G. H. Wu, H. Y. Liu, F. B. Meng, H. Z. Luo, and Y. X. Li, Eur. Phys. Lett. **91**, 17003P1–P5 (2010).
[17] A. Aryal, A. Quetz, S. Pandey, T. Samanta, I. Dubenko, M. Hill, D. Mazumdar, S. Stadler, and N. Ali, Journal of Alloys and Compounds **709**, 142–146 (2017).
[18] A. Aryal, A. Quetz, S. Pandey, I. Dubenko, S. Stadler, and N. Ali, Advances in Condensed Matter Physics **2017** (2017).
[19] J. Kamarad, F. Albertini, Z. Arnold, S. Fabbrici, and J. Kastil, Acta Materialia **77**, 60 (2014).
[20] H. W. Zhang, F. Wang, T. Y. Zhao, S. Y. Zhang, J. R. Sun, and B. G. Shen, Phys. Rev. B **70**, 212402 (2004).
[21] E. Bonnot, R. Romero, L. Manosa, E. Vives, and A. Planes, Phys. Rev. Lett. **100**, 125901 (2008).