Magnetic anisotropy and spin disorder in textured MnBi crystals synthesized by a field-inducing approach at a high temperature

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Textured MnBi crystals in a Bi matrix are fabricated by quenching at a high temperature ($\sim$653 K) in a magnetic field of 10 T. Microstructure observations reveal that MnBi grains are aligned along their *c*-axis. Magnetization measurements show a pronounced magnetic anisotropy in directions normal and parallel to the fabrication field resulting from the alignment. MnBi crystals display spin-disorder behaviors in ac magnetization, which may emerge due to the quenching processing. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2966456]

I. INTRODUCTION

Considerable efforts have been made to investigate the dependence of high magnetic field on structures and properties in the field of condensed matter or materials physics. It is often necessary to fabricate some magnetic materials with grains aligned in specific directions not only for fundamental understandings but also for engineering applications.[1] For example, large magnetic anisotropy in hard magnetic materials is desirable.[2] Recently, many efforts have been focused on the physics mechanism of magnetic field-induced transition, which is actually one of the most interesting problems in condensed matter physics and materials science.[3–7] Up to date, the physical origins of the magnetic field-induced transition, such as the definite mechanism of crystal growth and magnetic transition, are still not clear.

The binary compound MnBi, which shows high uniaxial magnetic anisotropy under low temperature phase (LTP) and excellent magneto-optical effect in its thin ferromagnetic (FM) films, has been widely investigated.[8–13] In the field of engineering, it is very potential to use MnBi as a hard magnet at high temperatures. This material can also be used as a permanent phase in nanocomposite magnets because the coercivity of the LTP MnBi increases with temperature.[9] A magnetocrystalline anisotropy of 9 T and a coercivity of 1.8 T have been reported at 550 K for the melt-spun ribbons.[14] The MnBi film possesses high magneto-optical properties due to its high Kerr rotation.[10] Magnetic moments of MnBi rotate from being parallel to the *c*-axis toward the basal plane of MnBi at a temperature of $\sim$90 K, i.e., a spin-reorientation transition (SRT) appears. The spin-orbit interaction plays a dominant role in the anisotropy of MnBi (LTP) during SRT.[8,15] Previously, we reported that MnBi crystals (T_c $\sim$628 K) can be magnetically aligned in a Bi matrix below T_c. The *H*-*T* phase diagram for the LTP MnBi was also reported in our previous article.[16,17] Composites fabricated by cooling through 535 K under magnetic fields of 0.3, 0.5, and 1.0 T show the improvement on crystal structures for both the LTP MnBi and the Bi matrix. Meanwhile, the increase in magnetic-alignment factor, spin-reorientation temperature, and magnetization ratio is found. Generally the gains in the above composites are maximized in the case of H_f=0.5 T. Here, H_f is defined as the fabrication field, i.e., the applied magnetic field during processing. Hence, composites produced under 0.5 T can be regarded as incorporating the best quality LTP MnBi crystals that could be prepared using this magnetic field alignment approach. In this article, magnetic field-induced alignment effect is employed to study self-assembling Bi–Mn alloys. Our experimental results show that a high magnetic field of 10 T can induce macroscopic order at a high temperature of 653 K. The magnetic anisotropy and spin disorder for textured MnBi crystals in a Bi matrix are investigated.

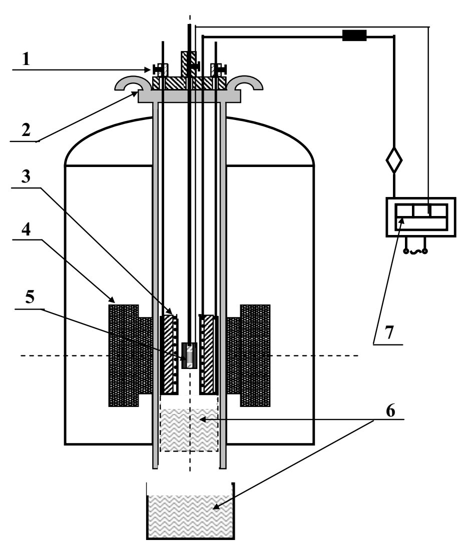

FIG. 1. Schematic diagram of experimental setup for sample preparation. (1) sample frame, (2) water-cool copper set, (3) heat furnace, (4) superconductor magnet, (5) sample, (6) water barrel for quenching, and (7)temperature control system.

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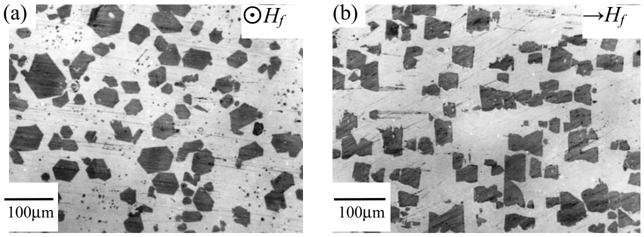

FIG. 2. Optical images showing effects of fabrication field on microstructures of MnBi–Bi composite. (a) Section perpendicular to and (b) section parallel to the fabrication field H_f.

II. EXPERIMENTAL DETAILS

Bi-6 wt % Mn alloys were prepared using bismuth (99.0%) and electrolytic manganese (99.5%). The alloys were melted in an inductive furnace and cast to graphite molds under argon ambience at a pressure of 50.6 kPa. Samples with 9.5 mm diameter and 25 mm length were sealed in graphite tube and inserted into a resistance furnace placed between two poles of the magnet, as shown in Fig. 1. The intensity of the magnetic field (up to 14 T) between poles of the magnet was adjusted and the temperature in the furnace chamber was controlled automatically. To study the field alignment above T_c, the alloys were heated up at a rate of 10 K/min to 653 K, maintained for 30 min in a magnetic field of 10 T, and then quenched in water (denoted as the Q-10 T sample). More details for sample preparation could be found in our previous paper.[16] Structures of the samples were characterized by optical microscopy and x-ray diffraction (XRD) with Cu $K\alpha$ radiation, respectively. Magnetic measurements were performed by using a physical properties measurement system (Quantum Design).

III. RESULTS AND DISCUSSION

Figure 2 shows the microstructures of the sample quenched at 653 K under the fabrication field of 10 T observed by optical microscopy. The regular hexagonal MnBi grains in the composite only appear in the section perpendicular to the fabrication field H_f [Fig. 2(a)], while the quadrilateral MnBi crystals (dark gray) in the Bi matrix (white) are present in the section parallel to the fabrication field [Fig. 2(b)]. The longer aligned MnBi crystals are not found in the Q-10 T sample quenched under 10 T. This may be due to the strong thermal fluctuation at high temperature (653 K), which results in the suppression of the further growth of crystals. However, the samples with better MnBi grain alignment can be obtained in a proper magnetic field (0.5 T), which is synthesized by solidifying at a low temperature (below 548 K).[16]

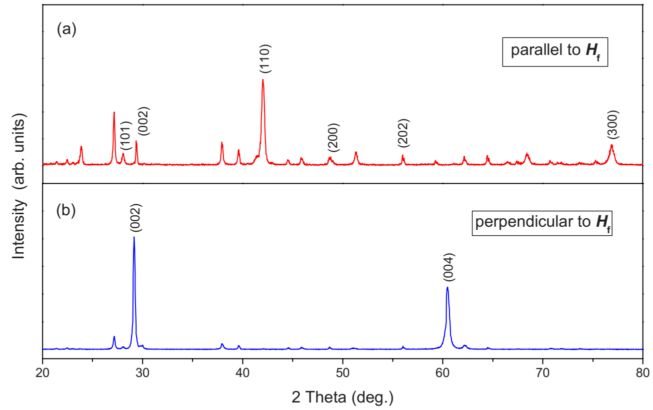

FIG. 3. (Color online) XRD patterns of samples quenched at the fabrication field H_f=10 T: (a) section parallel to H_f and (b) section perpendicular to H_f. Reflection peaks labeled by (hkl) are for MnBi and others for Bi.

To study the crystallographic texture of the sample, XRD measurement is performed along and normal to H_f. Figure 3 shows XRD patterns for the sample quenched at the fabrication field of H_f=10 T. XRD patterns indicate the formation of MnBi–Bi composite, which is also confirmed by energy dispersive x-ray analysis. For the section parallel to H_f [Fig. 3(a)], the (110), (200), and (300) Bragg reflections of MnBi phase appear stronger, compared to those for the section perpendicular to H_f [Fig. 3(b)]. For the latter, the (002) and (004) Bragg reflections are noticeably stronger instead. Obviously, MnBi crystals tend to orient their c-axis along the magnetic field of H_f at a temperature of above T_c. Due to

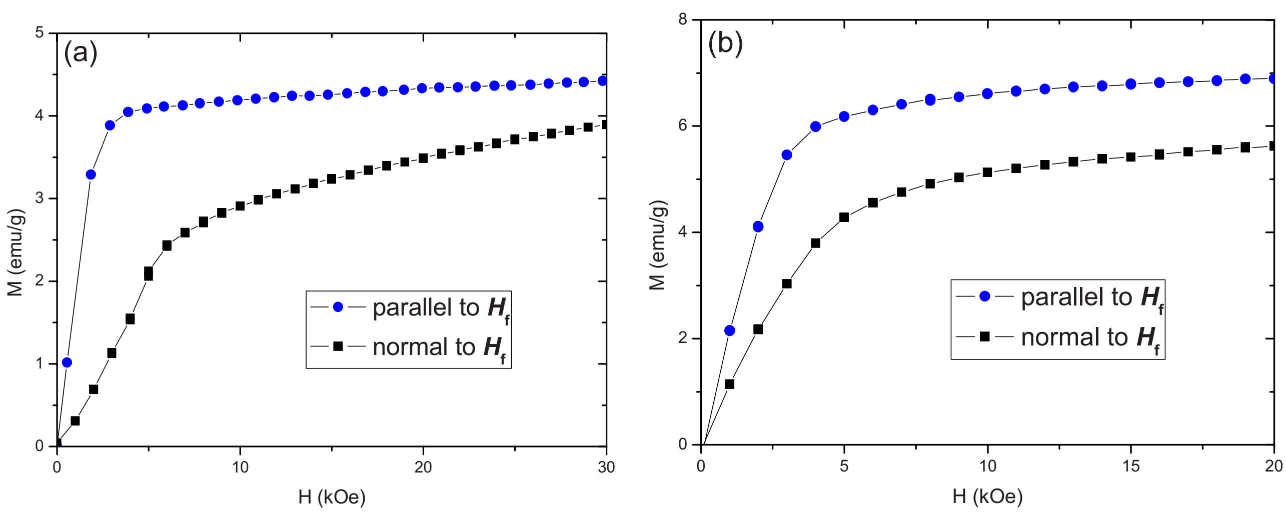

FIG. 4. (Color online) Magnetizations of samples quenched at 10 T, which are measured parallel to and normal to the fabrication field H_f at (a) 300 and (b) 50 K, respectively.

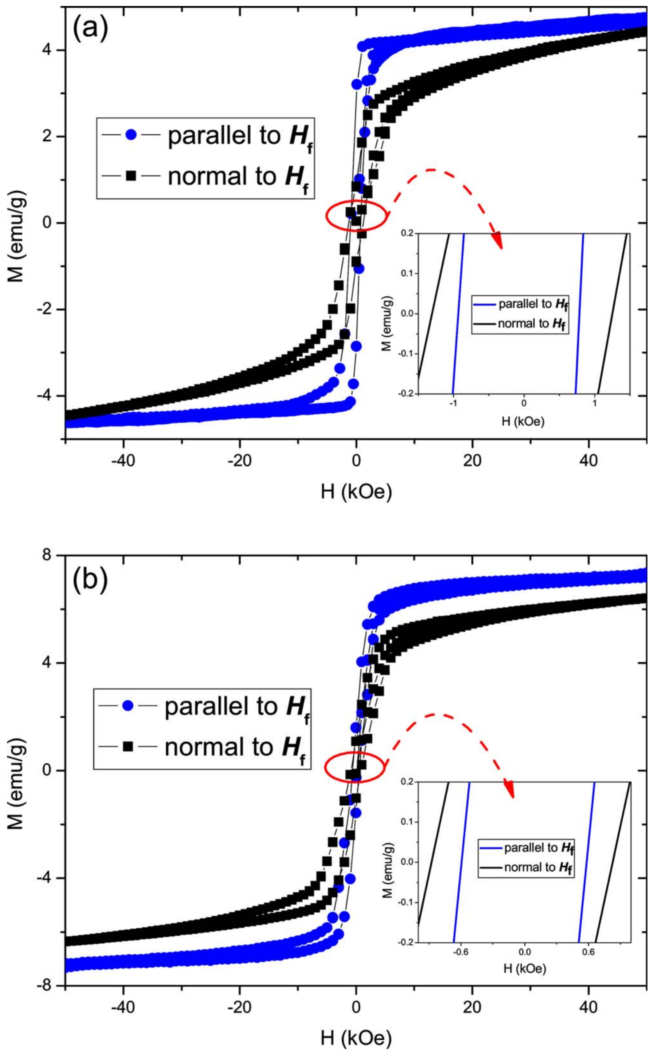

FIG. 5. (Color online) Hysteresis loops of samples quenched at 10 T, which are measured parallel to and normal to the fabrication field H_f at (a) 300 and (b) 50 K, respectively. Two insets show the enlarged regions close to the coercive field in two loops at 300 and 50 K, respectively.

quenching, the crystal quality of MnBi–Bi composites is worse than that of the solidifying samples. In comparison to a bonded magnet, where magnetic powders are aligned in magnetic fields and fixed with epoxy resins,[8] the textured MnBi crystals produced by the present method show a prominent feature, i.e., not only the alignment along the c-axis but also the large grains. It is more important that the present method can prevent the composition segregation of alloys, which gives rise to *in situ* alignment of crystals. Thus, it is expected to obtain the interesting structural and magnetic properties in the quenching sample.

It is understandable for the magnetic-alignment procedure to be well below T_c. It is hard to determine whether it is possible to magnetically align MnBi crystals at a high temperature, especially above T_c (the absence of FM phases). MnBi is FM and easily magnetized along the c-axis below T_c. According to the phase diagram of Bi–Mn system, there is a mix of solid high-temperature phase MnBi and liquid Bi in the temperature range from T_c to 719 K. During the heating process, T_c of MnBi increases from 628 K (0 T) to nearly 650 K under an applied magnetic field of 10 T.[17] Hence, the temperature of 653 K is quite critical since it is very close to T_c under 10 T. The ratio of the saturation magnetization between the Q-10 T sample and a reference sample (the completely FM MnBi) is ~25%. It means that about 25% of the sample volume has been transformed from the paramagnetic (PM) into the FM state isothermally during 30 min in the 10 T magnetic field, while about 75% of the sample volume remains in the PM state. PM and FM phases coexist in the Q-10 T sample, leading to a magnetically heterogeneous system in a chemically homogeneous specimen. With the coexistence, MnBi can be magnetically induced to rotate in viscous Bi liquid. Thus MnBi grains are oriented along the direction of the magnetic field since there is the interaction between the applied magnetic field and the strong magnetic moment induced from the FM state.

In the viscous liquid, the torque induced by the applied field on each MnBi particle can be calculated on the basis of the magnetic moment from MnBi compound. At a higher temperature, a larger magnetic field is necessary to enhance T_c, overcome strong thermal fluctuation, and then rotate MnBi particle. In the case of Bi-6 wt % Mn alloys, a magnetic field of 10 T is strong enough to align MnBi in the Bi matrix at 653 K. On the other hand, the magnetic dynamics near T_c is also important to understand the mechanisms of the alignment. Several factors, which may affect the magnetic dynamics, are the particle magnetic moment, temperature, and the strength of the applied field. Further experiments and analyses are ongoing.

To determine the anisotropy in magnetic properties, the samples were cut in such a way that the magnetization measurement could be performed from two directions, i.e., magnetizations parallel and perpendicular to the direction of the fabrication field. Figure 4 shows the magnetization curves for the Q-10 T sample (quenched under 10 T) at temperatures of (a) 300 and (b) 50 K. The magnetization curves

TABLE I. Sample name, fabrication field, fabrication temperature, coercive field along fabrication field, anisotropy field, and alignment factor for the samples studied.

Sample name	Fabrication field (T)	Fabrication temperature (K)	Coercive field at 300 K (Oe)	Anisotropy field at 300 K (Oe)	Alignment factor
The 0 T sample	0	Solidifying from 548 K	2735	1000	0.5
The 0.3 T sample	0.3	Solidifying from 548 K	1567	35 000	0.6
The 0.5 T sample	0.5	Solidifying from 548 K	1496	50 000	0.93
The 1 T sample	1	Solidifying from 548 K	1382	48 000	0.92
The Q-5 T sample	5	Quenching at 653 K	294	1600	0.5
The Q-10 T sample	10	Quenching at 653 K	842	60 000	0.9

exhibit the pronounced differences between the applied field parallel and perpendicular to the direction of the alignment. The magnetization curves along the direction of H_f are easier to saturate than those normal to the direction of H_f. Anisotropy fields for the sample at 50 and 300 K are about 9 and 6 T, respectively. This experimental result suggests that there exists a very strong anisotropy in the MnBi compound, and the anisotropy field decreases with increase in temperature.

In Fig. 5, hysteresis loops of the Q-10 T sample measured at 50 and 300 K are displayed, respectively. The coercive field H_c perpendicular to H_f is a bit larger than that parallel to H_f, which can be seen in the insets. This behavior is different from what is observed in MnBi films and bulk materials. Even if the crystallites are not entirely c-axis oriented, the coercivity should be larger along the easy axis. The exact mechanism for the behavior of H_c is not completely understood on the basis of the present experimental results. A possible explanation is that the magnetization reversal in the uniaxial Q-10 T sample takes place nearly exclusively by the displacement of domain walls. A similar behavior of H_c occurs as well in such uniaxial materials.[2] On the other hand, the quench processing in high magnetic field will induce stress anisotropy and defects anisotropy. The stress anisotropy and defects anisotropy affect reversible magnetization rotation and irreversible displacement of domain walls for oriented MnBi particles with uniaxial anisotropy. So they can also affect the coercivity. It can be also found that the remanent magnetization M_r parallel to H_f is larger than that perpendicular to H_f, as shown in Fig. 5. Both parallel and perpendicular to H_f, the saturation magnetization M_s decreases, but H_c and M_r increase with the increase in temperature. Interestingly, H_c and M_r are apparently presented at 50 K for the Q-10 T sample while they are hardly observed for the 0.5 T sample.[16]

For a material with uniaxial crystal structure, the alignment factor $\eta = M_r/M_s$ (where M_r is the remanent magnetization along the H_f and M_s is the saturation magnetization) should have a value ranging from 0.5 (corresponding to a completely random distribution) to 1.0 (corresponding to a perfect alignment).[18] Since η can serve as a good measure for the degree of particle alignment, it is used to reflect the degree of MnBi crystal alignment in this paper. There is a successful alignment of MnBi crystal for the Q-10 T sample since it reaches an alignment factor of 0.9, which is consistent with results for the 0.5 and 1.0 T samples (see Table I). In order to compare the other effects of processing factors, the related properties for various samples are also listed in Table I. It can be seen that the coercive field at 300 K decreases with the increase in fabrication field in the case of solidification from 548 K. However, the anisotropy field at 300 K and the alignment factor raise reach a saturation value at a fabrication field of 0.5 T. Interestingly, the coercive field, the anisotropy field, and the alignment factor all increase with the fabrication field in the case of quenching from 653 K. The coercive field in the quenching sample is much smaller than that in the solidifying one with a similar extent in alignment. The anisotropy field in the quenching samples, however, is slightly larger than that in the solidifying ones. It is possible that the quenching process causes some amorphous phases and the smaller coercive field. The large anisotropy field can be attributed to the pinning effect during quenching.

In order to further understand the magnetization behavior of the Q-10 T sample, a.c. susceptibility is investigated. Figure 6(a) shows the temperature dependence on the real

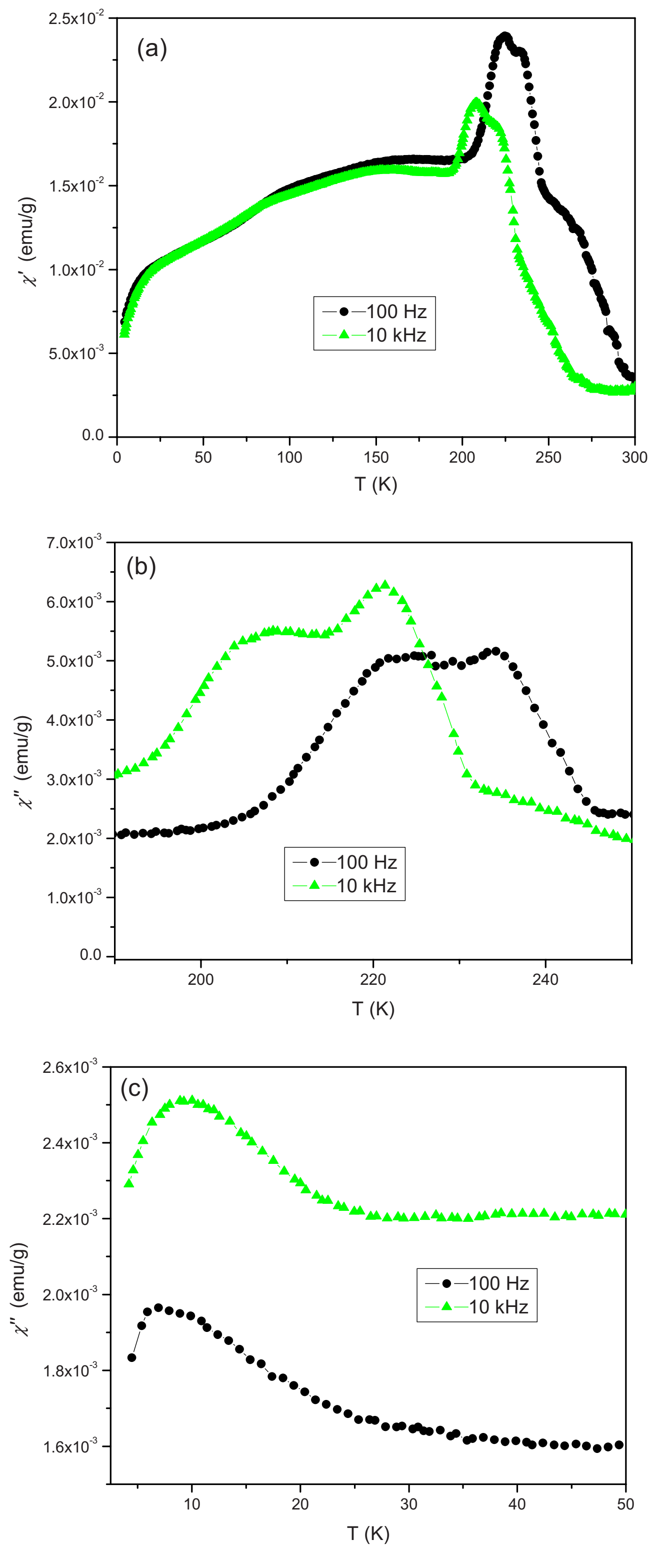

FIG. 6. (Color online) Temperature dependence of a.c. susceptibility for the Q-10 T sample at 100 Hz and 10 kHz. (a) The real (χ') component, (b) the imaginary (χ'') component in the temperature range from 180 to 260 K, and (c) the imaginary (χ'') component in the temperature range from 2 to 50 K.

(χ') component of the ac susceptibility at 100 Hz and 10 kHz, respectively. The $\chi'(T)$ curve displays a quasi-double-peak at temperatures of $\sim$208 and $\sim$225 K, respectively. The corresponding frequencies are 10 kHz and 100 Hz, respectively. The peak of temperature shifts toward low temperatures, while the height of the susceptibility peak diminishes with increasing frequency. In addition, there is a decreasing trend at $\sim$10 K. To further show the changes at the given temperature of 10 K as well as the peak temperature, the temperature dependence of the imaginary (χ'') component of the a.c. susceptibility is given in Figs. 6(b) and 6(c). It reveals that the quasi-double-peak in Fig. 6(a) turns into a two-hump in Fig. 6(b). The two-hump temperature also shifts toward low temperatures, but the height of the susceptibility peak increases with the increasing of frequency. In Fig. 6(c), the $\chi''(T)$ curve interestingly exhibits a new hump at 7.6 K under 100 Hz and at 9.7 K under 10 kHz, respectively. With the increasing of frequency, the hump temperature shifts toward high temperatures. As well known, in a spin glass system, the sharp cusp in the a.c. susceptibility occurs, the peak temperature shifts toward high temperatures, and the height of the susceptibility peak diminishes with the increasing of frequency.[19,20] Although present results are not consistent with them, we suppose that the studied MnBi system may have a slight amount of spin-disorder phases formed during the quenching process. The peak and/or hump are not so sharp, implying that FM order is formed.

IV. CONCLUSION

In the present work, a high-field processing approach has been employed to align MnBi crystals in the Bi matrix at a high temperature ($\sim$653 K). As a result of coexistence of PM and FM phases near to T_c, MnBi can be magnetically induced to rotate in the viscous Bi liquid. Both optical micrographs and XRD results have shown the clear evidence of magnetic alignment. Due to the induced enhancement of T_c and strong magnetic moments from the FM MnBi, the high magnetic field of 10 T is sufficient to rotate the MnBi in the viscous Bi liquid at a high temperature. The magnetization behaviors show pronounced anisotropy that results from the alignment of crystals. For two directions, parallel and perpendicular to the fabrication field, the coercive field and the remanent magnetization increase with the increase in temperature. There are apparent coercive field and remanent magnetization at 50 K for the quenching sample, which is different from results for the magnetic solidifying sample. The ac susceptibility measurements reveal some spin-disorder phases existing in the samples, which may result from the quenching process.

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[1] A. Geim, Phys. Today **51**(9), 36 (1998).
[2] S. Chikazumi, *Physics of Ferromagnetism*, 2nd ed. (Clarendon, Oxford, 1997).
[3] S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, Nature (London) **410**, 908 (2001).
[4] Y. Ma, S. Awaji, K. Watanabe, M. Matsumoto, and N. Kobayashi, Solid State Commun. **113**, 671 (2000).
[5] Y. Shimamoto, N. Miura, and H. Nojiri, J. Phys.: Condens. Matter **10**, 11289 (1998).
[6] E. Levin, K. Gschneidher, Jr., and V. Pecharsky, Phys. Rev. B **65**, 214427 (2002).
[7] B. Lake, H. Ronnow, N. Christensen, G. Aeppli, K. Lefmann, D. Mcmorrow, P. Vorderwisch, P. Smeibidl, N. Mangkorntong, T. Sasagawa, M. Nohara, H. Takagi, and T. Mason, Nature (London) **415**, 299 (2002).
[8] J. Yang, K. Kamaraju, W. Yelon, and W. James, Appl. Phys. Lett. **79**, 1846 (2001).
[9] K. Kang, L. Lewis, and A. Moodenbaugh, Appl. Phys. Lett. **87**, 062505 (2005).
[10] K. Harder, D. Menzel, T. Widmer, and J. Schoenes, J. Appl. Phys. **84**, 3625 (1998).
[11] T. Chen and W. Stutius, IEEE Trans. Magn. **10**, 581 (1974).
[12] S. Saha, R. Obermyer, B. Zande, V. Chandhok, S. Simizu, S. Sankar, and J. Horton, J. Appl. Phys. **91**, 8525 (2002).
[13] Y. Xu, B. Liu, and D. Pettifor, Phys. Rev. B **66**, 184435 (2002).
[14] X. Guo, X. Chen, Z. Altounian, and J. Strom-Olsen, Phys. Rev. B **46**, 14578 (1992).
[15] R. Coehoorn and R. De Groot, J. Phys. F: Met. Phys. **15**, 2135 (1985).
[16] Y. Liu, J. Zhang, S. Cao, G. Jia, X. Zhang, Z. Ren, X. Li, C. Jing, and K. Deng, Phys. Rev. B **70**, 184424 (2004).
[17] Y. Liu, J. Zhang, S. Cao, G. Jia, X. Zhang, Z. Ren, X. Li, C. Jing, and K. Deng, Phys. Rev. B **72**, 214410 (2005).
[18] S. Liu, J. Appl. Phys. **76**, 6757 (1994).
[19] I. Skorvanek, S. Skwirblies, and J. Kotzler, Phys. Rev. B **64**, 184437 (2001).
[20] I. Suzuki and M. Suzuki, Phys. Rev. B **73**, 094448 (2006).