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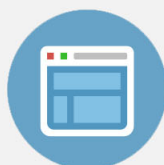
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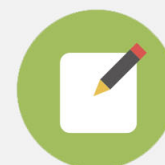


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Development of MnBi permanent magnet: Neutron diffraction of MnBi powder

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MnBi attracts great attention in recent years for its great potential as permanent magnet materials. MnBi phase is difficult to obtain because of the rather drastic peritectic reaction between Mn and Bi. In this paper, we report our effort on synthesizing high purity MnBi compound using conventional powder metallurgical approaches. Neutron diffraction was carried out to investigate the crystal and nuclear structure of the obtained powder. The result shows that the purity of the obtained powder is about 91 wt. % at 300 K, and the magnetic moment of the Mn atom in MnBi lattice is 4.424 and 4.013 μ_B at 50 K and 300 K, respectively. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4867230>]

I. INTRODUCTION

MnBi based magnet is an attractive alternative to the permanent magnets containing rare earth elements, especially the ones for medium temperature applications (423–473 K) such as NdFeB-Dy and SmCo. MnBi has unique temperature properties: its coercivity increases with increasing temperature, reaching a maximum of 2.5 T at 540 K.^{1–4} The large coercivity is attributed to MnBi's large magnetocrystalline anisotropy (1.6×10^6 J/m³).⁵ However, MnBi has relatively low magnetization. Its room temperature saturation magnetization is about 75 emu/g or 8.4 kG with 5 T field.⁶ The roadmap for developing a MnBi-based exchange-coupled magnet starts with preparing high purity MnBi compound in large quantity. Synthesizing MnBi is a challenge. A rather drastic peritectic reaction exists over wide temperature and composition ranges. Several methods have been utilized in preparation of high purity MnBi single phase, including arc-melting, sintering, and melt-spin rapid solidification.^{4,7–10} Among them, only rapid solidification was able to consistently produce over 90% pure MnBi single phase. However, a conventional method such as casting followed by heat treatment is much preferred because of its compatibility with the current industrial practice. A recent result by Hadjipanayis' group shows that the conventional cast-anneal method has the potential to achieve 90% single phase material.¹¹ Similar methods were investigated by the author's group. Nuclear and magnetic structures of the obtained MnBi phase were investigated using neutron diffraction techniques. The results are reported in this paper.

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II. EXPERIMENTAL METHODS

MnBi powder was prepared using arc melting followed by thermal-mechanical purification process involving grind-and-sieve and annealing. Raw materials Mn chips and Bi shots were purchased from Aldrich (SKU 26617 and 556130, respectively). The Mn chips and Bi shots were mixed in approximately 56:44 atomic ratio. The mixture was arc-melted three times to achieve homogeneity. The obtained ingot was crushed and ground into powder using mortar and pestle, and sieved using #325 mesh screens resulting in particles with average sizes of 44 μm . The obtained powder was annealed at 563 K for 24 h in vacuum furnace with 10 mTorr backing pressure. Neutron powder diffraction data were collected in the 50–500 K temperature range on the BT-1 high-resolution neutron powder diffractometer at NIST Center for Neutron Research using a Cu (311) monochromator with wavelength of 1.5403 Å. The intensities were measured with 0.05° scanning step size in the 2θ range of 3°–165°. Crystal and magnetic structures were refined with the General Structure Analysis System program.¹² The neutron scattering amplitudes used in refinements were 0.375 and 0.853 ($\times 10^{-12}$ cm) for Mn and Bi, respectively. The sample was sealed in a cylindrical vanadium container filled with He exchange gas. Temperature dependent magnetization of the obtained powder was measured using a Physical Property Measurement System (PPMS) by Quantum Design. The system holds the applied field at 9 T constant while ramping the temperature from 10 to 400 K, then back to 10 K.

III. RESULTS AND DISCUSSION

The obtained powder was analyzed for crystal structure and phase content using neutron powder diffraction. MnBi,

TABLE I. Reitveld refinement results.

Temperature (K)	50	100	150	200	250	300	350	400	500
Nuclear phases weight fraction (%)									
MnBi	91.3%	90.7%	91.0%	90.5%	90.7%	91.1%	90.8%	89.9%	86.4%
Mn	4.8%	5.6%	5.0%	5.5%	5.3%	5.2%	5.4%	5.6%	5.1%
Bi	3.9%	3.7%	4.0%	4.1%	3.9%	3.7%	3.7%	4.5%	8.4%
Lattice parameter (Å)									
MnBi, a	4.2764	4.2801	4.2833	4.2862	4.2891	4.2909	4.2937	4.2965	4.3014
±	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0002
MnBi, c	6.0724	6.0813	6.0911	6.1044	6.1165	6.1234	6.1350	6.1455	6.1635
±	0.0001	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0003	0.0003
Mn	8.8873	8.8891	8.8972	8.9064	8.9145	8.9212	8.9309	8.9404	8.9611
±	0.0005	0.0008	0.0008	0.0008	0.0008	0.0006	0.0008	0.0008	0.0010
Bi, a	4.5327	4.5341	4.5367	4.5403	4.5437	4.5465	4.5468	4.5527	4.5599
±	0.0016	0.0017	0.0016	0.0015	0.0014	0.0011	0.0016	0.0013	0.0009
Bi, c	11.8216	11.8457	11.8653	11.8826	11.8797	11.8718	11.8924	11.8798	11.9113
±	0.0095	0.0100	0.0090	0.0087	0.0081	0.0065	0.0091	0.0075	0.0049
Crystal structures: MnBi (P 63/mmc), Mn (I -4 3 m), Bi (R -3 m H)									
Magnetic moment (μ_B)									
Mn	4.424	4.527	4.42	4.307	4.122	4.013	3.895	3.703	3.393
±	0.030	0.039	0.043	0.043	0.042	0.032	0.045	0.046	0.057
Mn, Mx	4.424	3.064	1.409	0.544	0	0	0	0	0
±	0.030	0.085	0.164	0.406	0	0	0	0	0
Mn, My	0	0	0	0	0	0	0	0	0
±	0	0	0	0	0	0	0	0	0
Mn, Mz	0	3.332	4.19	4.273	4.122	4.013	3.895	3.703	3.393
±	0	0.068	0.057	0.055	0.042	0.032	0.045	0.046	0.057
θ	90°	42.60°	18.584	7.253	0	0	0	0	0
±	0	1.29°	2.18	5.421	0	0	0	0	0

Mn, and Bi are the three phases used to fit the diffraction pattern. Phase fractions, lattice parameters, and magnetization moments are listed in Table I.

Saturation magnetization of the MnBi powder was measured with 9 T applied field while ramping the temperature from 10 to 400 K, then back to 10 K. The M-T curve is shown in Figure 1. The maximum saturation magnetization, M_S , of the MnBi powder measured 81.2 emu/g at about 80 K. Beyond 80 K, the M_S decreases monotonically with increasing temperature. From 200 to 400 K, the decrease of M_S is nearly linear, at a rate of about 0.055 emu/(g K). The

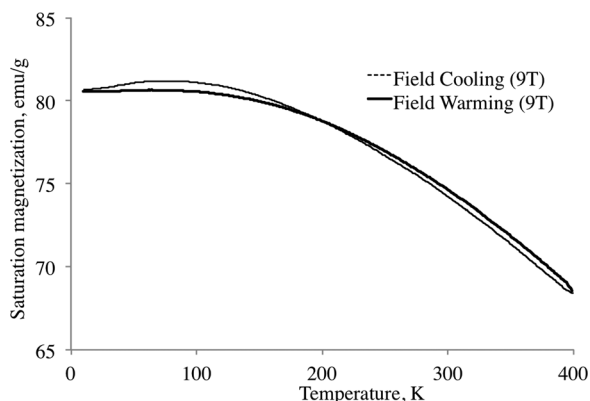


FIG. 1. Saturation magnetization of the MnBi powder as a function of temperature. During the temperature ramping, the applied magnetic field is kept constant at 9 T.

maximum at 80 K can be explained by a simple mean field model. The magnetization M of MnBi increases with volume V , as we find from density functional theory calculations performed at 0 K. Near 0 K, there are few competing phenomena and the small increase found in the measured $M(V(T))$ is simply due to thermal expansion, $V(T)$. Indeed, a simple model of the magnetization near 0 K yields a Brillouin function behavior with direct $V(T)$ dependence that weakly enhances $M(T)$, which is then quickly overwhelmed by spin thermal disordering resulting in decrease of M at increasing T . The phenomenon is general. Mathematically, both the function $M(V)$ and the functional $M(V(T))$ have positive slopes; yet, the thermal disordering of local spins is described by a smooth nonlinear magnetization curve with negative curvature and zero slope at $T=0$ K; this reduction of magnetization is negligible at low T and dominates at higher T . From the combination of these two effects, the magnetization of a thermally expanding sample first weakly increases and then decreases with T , with an experimentally observed maximum around $T=80$ K.

Based on the phase fraction results obtained by neutron diffraction (91.1% MnBi) and the magnetization data obtained by PPMS (80.5, 81.2, 74, and 68.5 emu/g at 10, 80, 300, and 400 K, respectively), the magnetizations of pure MnBi low-temperature phase can be calculated as 88.5, 89.2, 81.3, and 75.3 emu/g at 10, 80, 300, and 400 K, respectively. This is equivalent to 4.18, 4.24, 3.84, and 3.56 μ_B per Mn-Bi pair at these temperatures. The result agrees with Anderson's

1972 data ($4.18 \mu_B$ at 10 K)¹³ and is in close agreement with Yang's 2011 data (4.23, 4.1, 3.7, and $3.55 \mu_B$ at 10, 100, 300, and 400 K, respectively).³

IV. CONCLUSIONS

MnBi is good hard phase because of its high coercivity (~ 2 T at 473 K). Unfortunately, MnBi has a relatively low magnetization. Its saturation magnetization decreases from 81 emu/g to 65 emu/g when temperature increases from 100 K to 473 K. Consequently, the theoretical maximum energy product, $(BH)_{\max}$, decreases from 20 to 13 MGOe. To meet the benchmark of 20 MGOef at 473 K set by NdFeB-Dy, about 20 vol. % of soft phase such as cobalt must be exchange coupled to MnBi.

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- ¹Y. B. Yang, X. G. Chen, S. Guo, A. R. Yan, Q. Z. Huang, M. M. Wu, D. F. Chen, Y. C. Yang, and J. B. Yang, *J. Magn. Magn. Mater.* **330**, 106 (2013).
- ²J. B. Yang, W. B. Yelon, W. J. James, Q. Cai, M. Kornecki, S. Roy, N. Ali, and P. l'Heritier, *J. Phys.: Condens. Matter* **14**, 6509 (2002).
- ³J. B. Yang, Y. B. Yang, X. G. Chen, X. B. Ma, J. Z. Han, Y. C. Yang, S. Guo, A. R. Yan, Q. Z. Huang, M. M. Wu, and D. F. Chen, *Appl. Phys. Lett.* **99**, 082505 (2011).
- ⁴J. B. Yang, K. Kamaraju, W. B. Yelon, W. J. James, Q. Cai, and A. Bollero, *Appl. Phys. Lett.* **79**, 1846 (2001).
- ⁵X. Guo, X. Chen, Z. Altounian, and J. O. Stromolsen, *Phys. Rev. B* **46**, 14578 (1992).
- ⁶Y. B. Yang, X. G. Chen, R. Wu, J. Z. Wei, X. B. Ma, J. Z. Han, H. L. Du, S. Q. Liu, C. S. Wang, Y. C. Yang, Y. Zhang, and J. B. Yang, *J. Appl. Phys.* **111**, 07E312 (2012).
- ⁷H. Yoshida, T. Shima, T. Takahashi, and H. Fujimori, *Mater. Trans. JIM* **40**, 455 (1999).
- ⁸X. Guo, A. Zaluska, Z. Altounian, and J. O. Stromolsen, *J. Mater. Res.* **5**, 2646 (1990).
- ⁹B. W. Roberts, *Phys. Rev.* **104**, 607 (1956).
- ¹⁰X. Guo, Z. Altounian, and J. O. Stromolsen, *J. Appl. Phys.* **69**, 6067 (1991).
- ¹¹N. V. R. Rao, A. M. Gabay, and G. C. Hadjipanayis, *J. Phys. D: Appl. Phys.* **46**, 062001 (2013).
- ¹²A. C. Larson and R. B. Von Dreele, "General structure analysis system (GSAS)," Los Alamos National Laboratory Report No. LAUR 86-748, 2004.
- ¹³A. F. Andresen, J. E. Engebretsen, and J. Refsnes, *Acta Chem. Scand.* **26**, 175 (1972).