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## Magnetic properties of the MnBi intermetallic compound

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A MnBi alloy containing over 90 wt% low-temperature phase (LTP) has been obtained by high-temperature sintering and magnetic purification. The coercivity of the bonded MnBi magnet increases with increasing temperatures. A coercivity of 2.0 T has been achieved at 400 K. The maximum energy product  $(BH)_{\max}$  of the magnet is 7.7 MGOe (61 kJ/m<sup>3</sup>) and 4.6 MGOe (37 kJ/m<sup>3</sup>) at room temperature and 400 K, respectively. Neutron diffraction and magnetic data reveal a spin reorientation, which gives rise to low anisotropy fields and coercivity at lower temperatures for the LTP MnBi alloy. © 2001 American Institute of Physics.

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The magnetic properties of the MnBi compound have been studied extensively due to the high uniaxial magnetic anisotropy ( $2.2 \times 10^7$  erg/cm<sup>3</sup> at 500 K) of its low-temperature phase (LTP),<sup>1,2</sup> and the magneto-optical properties of its quenched high-temperature phase,<sup>3</sup> which can be used in permanent magnets and magneto-optical memory devices. Heiks and Roberts have reported that LTP MnBi exhibits magnetic moments of 4.0 and 3.95  $\mu_B$ /Mn.<sup>4,5</sup> A magnetocrystalline anisotropy of 9.0 T and a coercivity of 1.8 T have been observed at 550 K, which is very interesting for high-temperature applications.<sup>6</sup> Adams, Hubbard, and Syeles have produced a MnBi magnet with a maximum energy product of 4.3 MGOe, which is much smaller than the theoretical value of 16 MGOe.<sup>7</sup> The formation of pure LTP MnBi is very difficult to achieve using conventional methods, such as sintering. Mn tends to segregate from the MnBi liquid because of the peritectic reaction, and the diffusion of Mn through MnBi is exceedingly slow.<sup>5,8</sup> Many efforts have been made to produce MnBi.<sup>7–16</sup> At present, no single-phase MnBi has been prepared by sintering Mn and Bi powders.<sup>4–12</sup> About 95 wt% LTP MnBi can be prepared by rapid quenching and subsequent heat treatments.<sup>15</sup> Yoshida *et al.*, have reported some MnBi with about 90 wt% single phase by arc melting under a He atmosphere.<sup>16</sup>

In this letter, we report that over 90 wt% LTP MnBi bulk samples can be produced by sintering and subsequent magnetic purification. The dependence of coercivity and anisotropy on the temperature has been studied using these high-purity materials. A coercivity of 2.0 T and a maximum energy product  $(BH)_{\max}$  of 4.6 MGOe have been obtained for MnBi-bonded magnets at 400 K. The magnetic structure of MnBi has been investigated by a combination of neutron diffraction techniques and magnetic measurements.

Figure 1 shows x-ray diffraction patterns taken at room

temperature with Cu  $K_\alpha$  radiation for a sintered MnBi sample before and after magnetic purification. It can be seen that the characteristic peaks of Bi dramatically decrease after magnetic separation of the two phases. Neutron diffraction data were collected using the position-sensitive diffractometer (wave length=1.4783 Å) at the University of Missouri–Columbia research reactor, to determine the magnetic structure of the MnBi alloys. The diffraction data were refined using the program FULLPROF, a program for Rietveld analysis.<sup>17</sup> Figure 2 shows the neutron diffraction pattern of MnBi after magnetic separation at room temperature. It is found there is approximately 90 wt% of LTP MnBi in the magnetically separated powders. The MnBi phase has a hexagonal structure with lattice parameters  $a=4.2827$  Å and  $c$

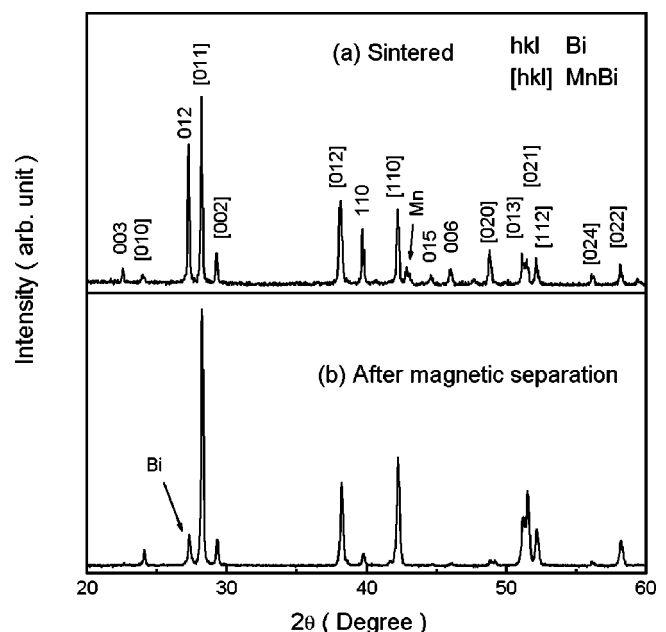


FIG. 1. X-ray diffraction patterns of sintered MnBi, before and after magnetic separation.

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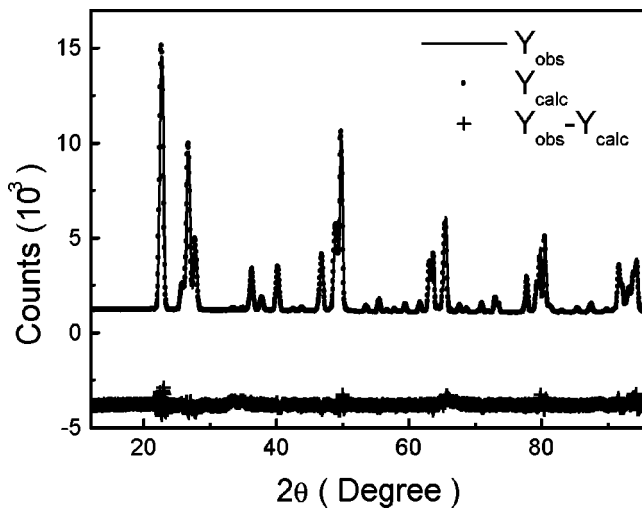


FIG. 2. Typical neutron diffraction pattern of MnBi at room temperature.

$=6.1103 \text{ \AA}$ , which correspond to the LTP phase.<sup>8,14</sup> The neutron data refinement shows that the manganese possesses a magnetic moment of  $3.60\mu_B$  at room temperature, which agrees well with the magnetic measurements on polycrystalline MnBi,<sup>4,6</sup> on single crystals,<sup>14</sup> and with theoretical band calculations.<sup>18</sup> This value is considerably less than that obtained by previous neutron diffraction measurements,<sup>5</sup> where a value of  $4.0\mu_B$  was claimed, likely due to the poor quality of the spectra and the sample purity. The formation of ferromagnetic LTP MnBi is essential for the preparation of permanent magnets because MnBi also exhibits several closely related phases along with LTP,<sup>15</sup> which are not ferromagnetic.

In order to get a high coercivity for MnBi, it is necessary to pulverize it into fine particles approaching domain size of an estimated critical diameter of about  $0.5 \mu\text{m}$ . The high-purity MnBi powders are mechanically ground for several hours and the fine powders are fixed into an epoxy resin and subjected to a magnetic field of about 1.0 T to form magnetically aligned samples of cylindrical shape. Figure 3 shows hysteresis loops of resin-bonded MnBi magnets measured at different temperatures. Coercivities of 2.0 and 0.004 T have been observed at 400 and 50 K, respectively. It is evident that the coercivity has a large temperature dependence, see Fig. 4. The coercivity rapidly increases with temperature from 150 to 400 K; an even larger coercivity than 2.0 T can be expected at higher temperature. The coercivities in the temperature range 220–300 K are much higher than the values obtained for samples prepared by melt spining,<sup>6</sup> which may be attributed to a different coercivity mechanism. Normally, in the melt spining over quenched ribbons, coercivity fields might be mainly produced by domain-wall pinning, while coercivity in our MnBi samples is controlled by nucleation hardening, which has been confirmed by magnetic-field dependence of the coercivity. The positive temperature coefficient of coercivity for MnBi magnets above room temperature is a great advantage relative to the present hard magnetic materials (Nd–Fe–B or Sm–Co magnets) with negative coefficients for application at high temperatures. Below 150 K, the coercivity tends to become zero due to the anisotropy change.<sup>14</sup> The maximum energy product  $BH_{\text{max}}$  of the magnet is 7.7 MGOe ( $61 \text{ kJ/m}^3$ ) and 4.6 MGOe ( $37 \text{ kJ/m}^3$ ) at

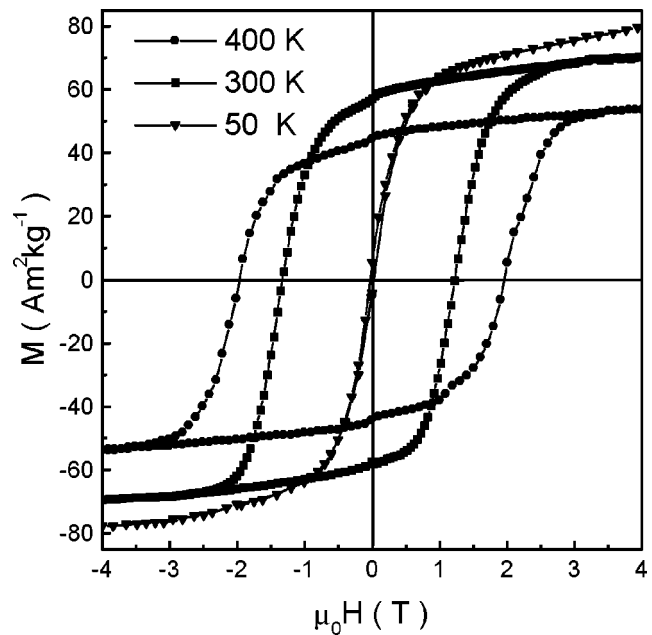


FIG. 3. Hysteresis loops of MnBi magnets at different temperatures.

room temperature and 400 K, respectively, which are the largest values reported so far for MnBi magnets.

Figure 5 shows the magnetization curves measured along a direction perpendicular to the aligned direction at different temperatures. As a comparison, we also include two magnetization curves measured parallel to the aligned direction at 400 and 50 K. It can be seen that the magnetization curves along the hard axis become easier to saturate when the temperature decreases, which indicates that the uniaxial anisotropy decreases with decreasing temperature, and tends to become plan anisotropy below 100 K. This may explain the decrease in coercivity with decreasing temperature. Figure 6 is the temperature dependence of the magnetization of the MnBi oriented along the  $c$  axis. The applied field is 2000 Oe. A sharp maximum, which is related to the spin reorien-

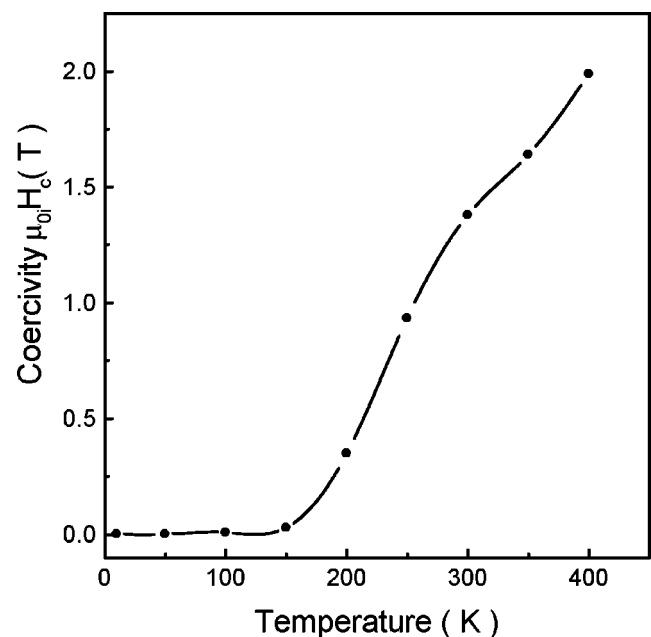


FIG. 4. Dependence of the coercivity on temperature for MnBi magnets.

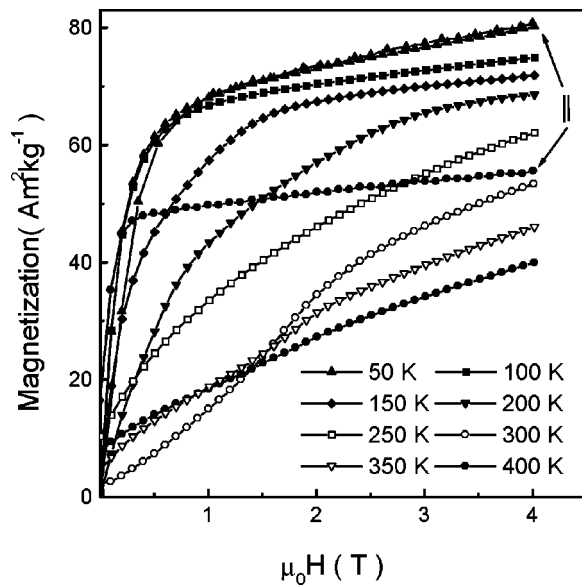


FIG. 5. Magnetization curves along a direction perpendicular to the aligned direction at different temperatures. (For comparison, two curves at 400 and 50 K along the *c* axis are included).

tation, is observed at 90 K. This has not been observed in the *M*–*T* curves of Heikes<sup>4</sup> and Chen and Stutius.<sup>14</sup> According to our neutron diffraction data and magnetic measurements at different temperatures, the magnetization of Mn is along the *c* axis from 240 to 650 K. It begins to deviate gradually from

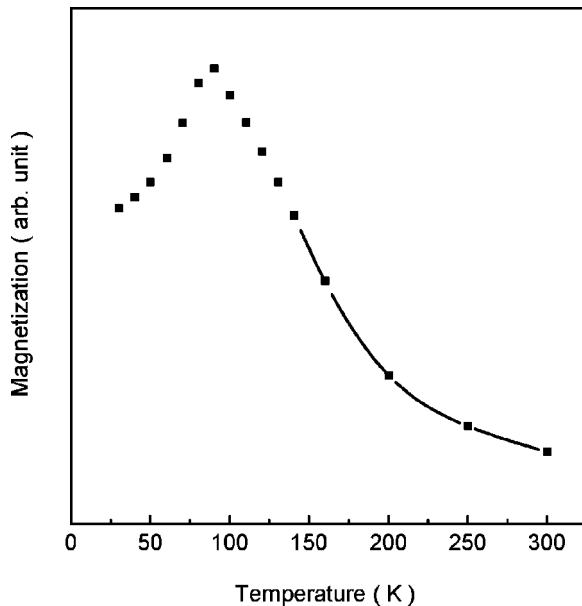


FIG. 6. Temperature dependence of the magnetization for MnBi along the *c* axis.

the *c* axis at about 200 K, and continues to approach the *ab* plane down to 50 K. The magnetization curves indicate that at 50 K the sample becomes more difficult to saturate compared with the case of 100 K (see Fig. 5). This suggests that an easy cone magnetic structure is formed at 50 K, which has been confirmed by our recent neutron data (to be published elsewhere). Coehoorn and De Groot<sup>18</sup> have reported that the spin-orbit interaction plays a key role in the anisotropy at low temperatures for MnBi, in as much as the magnetic dipole–dipole interaction cannot explain the low-temperature anisotropy. Further studies regarding the temperature dependence of the anisotropy of MnBi are in progress.

In conclusion, high-purity LTP MnBi has been synthesized and the structure and magnetic properties of LTP have been investigated. Magnetically hard LTP MnBi exhibits a positive temperature coefficient for coercivity, and the coercivity attains a value of 2.0 T at 400 K. A maximum energy product of 4.6 MGOe (37 kJ/m<sup>3</sup>) has been achieved at 400 K. A sharp maximum at about 90 K on the *M*–*T* curve clearly shows a spin reorientation. The change of anisotropy from uniaxial anisotropy at 400 K to nearly the *ab* plane below 50 K, is in accord with the decrease in coercivity.

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<sup>1</sup>C. Guillaud, J. Phys. Radium **12**, 143 (1951).

<sup>2</sup>W. E. Stutius, T. Chen, and T. R. Sandin, AIP Conf. Proc. **18**, 1222 (1974).

<sup>3</sup>D. Chen and Y. Gondo, J. Appl. Phys. **35**, 1024 (1964).

<sup>4</sup>R. R. Heikes, Phys. Rev. **99**, 446 (1955).

<sup>5</sup>B. W. Roberts, Phys. Rev. **104**, 607 (1956).

<sup>6</sup>X. Guo, X. Chen, Z. Altounian, and J. O. Ström-Olsen, Phys. Rev. B **46**, 14578 (1992).

<sup>7</sup>E. Adams, W. M. Hubbard, and A. M. Syeles, J. Appl. Phys. **23**, 1207 (1952).

<sup>8</sup>A. F. Andresen, W. Hälgl, P. Fisher, and E. Stoll, Acta Chem. Scand. (1947-1973) **21**, 1543 (1967).

<sup>9</sup>R. G. Pirich, Met. Trans. A **11A**, 193 (1983); IEEE Trans. Magn. **MAG-16**, 1065 (1980).

<sup>10</sup>R. G. Pirich and D. J. Larson, Jr., J. Appl. Phys. **50**, 2425 (1979).

<sup>11</sup>J. M. Noothoven van Goor and H. Zijlstra, J. Appl. Phys. **39**, 5471 (1968).

<sup>12</sup>A. F. Andresen, W. Hälgl, P. Fisher, and E. Stoll, Acta Chem. Scand. (1947-1973) **21**, 1545 (1967).

<sup>13</sup>S. Saha, M. Q. Huang, C. J. Thong, B. J. Zande, V. K. Chandhok, S. Simizu, R. T. Obermyer, and S. G. Sankar, J. Appl. Phys. **87**, 6040 (2000).

<sup>14</sup>T. Chen and W. Stutius, IEEE Trans. Magn. **MAG-10**, 581 (1974).

<sup>15</sup>X. Guo, A. Zaluska, Z. Altounian, and J. O. Ström-Olsen, J. Mater. Res. **5**, 2646 (1990).

<sup>16</sup>H. Yoshida, T. Shima, T. Takahashi, and H. Fujimori, Mater. Trans., JIM **40**, 455 (1999).

<sup>17</sup>J. Rodriguez-Carvajal, Program: FULLPROF, version 3.5d (1998).

<sup>18</sup>R. Coehoorn and R. A. De Groot, J. Phys. F: Met. Phys. **15**, 2135 (1985).