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# Structure and magnetic properties of the MnBi low temperature phase

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High purity MnBi low temperature phase has been prepared and analyzed using magnetic measurements and neutron diffraction. The low-temperature phase of the MnBi alloy has a coercivity $\mu_{0i}H_c$ of 2.0 T at 400 K, and exhibits a positive temperature coefficient from 0 to at least 400 K. The neutron data refinement indicated that the Mn atom changes its spin direction from *c* axis above room temperature to nearly perpendicular to the *c* axis at 50 K. A canted magnetic structure has been observed below 200 K. The anisotropy field increases with increasing temperature which gives rise to a high coercivity at the higher temperatures. The anisotropic bonded magnets have maximum energy products $(BH)_{\max}$ of 7.7 and 4.6 MGOe at room temperature and 400 K, respectively. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1451306]

## I. INTRODUCTION

MnBi is a ferromagnetic intermetallic with NiAs-type hexagonal crystal structure. MnBi has been of interest because of the unusually large magnetic anisotropy of the low-temperature phase (LTP)[1,2] and the favorable magneto-optical properties of the quenched high-temperature phase.[3] It is remarkable that the coercivity of the LTP increases with temperature, and is much larger than that of the Nd–Fe–B magnets at higher temperatures. Therefore, MnBi has considerable potential as a permanent magnet at high temperatures and as a hard phase in nanocomposite magnets.[4] A magnetocrystalline anisotropy of 9.0 T and a coercivity of 1.8 T have been measured at 550 K for the melt-spun ribbons, which is very interesting for high temperature applications.[4] Adam *et al.* 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.[5] The anisotropy constant decreases rapidly with decreasing temperature, where a spin reorientation has been observed.[6] However, no details have been reported. It is difficult to obtain single-phase MnBi materials by conventional methods, such as sintering, which also makes it difficult to study the magnetic properties of MnBi. Mn tends to segregate from the MnBi liquid because of the peritectic reaction, and the diffusion of Mn through MnBi is exceedingly slow.[7–9] Many efforts have been made to produce single phase MnBi.[7–15] At present, no single phase MnBi has been prepared by sintering Mn and Bi powders.

In order to fully understand the magnetic behavior of the MnBi, over 90 wt % LTP MnBi bulk samples have been produced by sintering and subsequent magnetic purification. The dependence of the coercivity and anisotropy on the temperature has been studied using these relatively 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.

## II. EXPERIMENTAL METHOD

High purity manganese (99.99%) and bismuth (99.99%) were mixed in atomic ratios of 40:60, 45:55, and 50:50. These mixtures were molded into a columnar shape under a pressure of 4000 kg/cm$^2$ and then sintered in an argon atmosphere for 1–10 h at 1000 °C followed by cooling to room temperature. The optimum composition is Mn:Bi = 55:45, where up to 60 wt % of LTP MnBi can be obtained after sintering. Magnetic separation was used to enrich the MnBi LTP in the powders. The MnBi powders were further ground to fine powders, and aligned in a 10 kOe field in an epoxy resin to form a bonded magnet. Magnetic measurements were performed with a field of up to 60 kOe in a temperature range from 4.2 to 400 K using a superconducting quantum interference device magnetometer. The samples were characterized for their phase purity by x-ray diffraction with Cu $K\alpha$ radiation. Neutron powder diffraction patterns were collected using the diffractometer at the University of Missouri Research Reactor at a wavelength of 1.4807 Å.

## III. RESULTS AND DISCUSSION

Structure and magnetic properties. Figure 1 is the neutron diffraction pattern of MnBi after magnetic separation at different temperatures. Refinements of the neutron diffraction data were carried out using FULLPROF,[16] which permits

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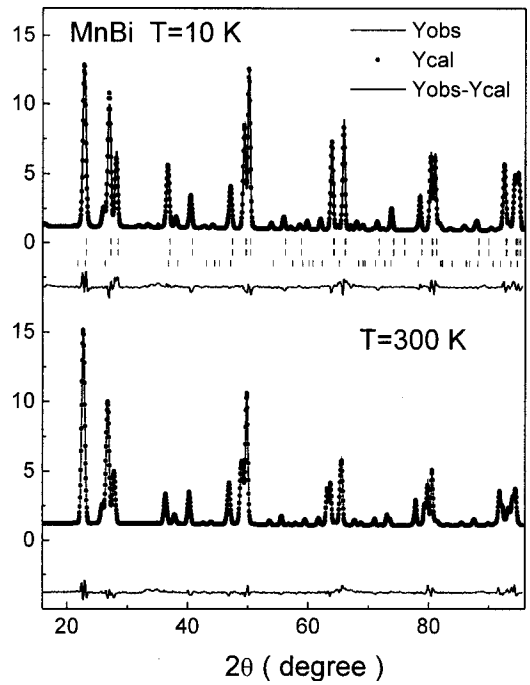


FIG. 1. Observed ($Y_{obs}$) and calculated ($Y_{cal}$) neutron diffraction patterns of MnBi at 10 K and room temperature. [The bottom curves ($Y_{obs}-Y_{cal}$) are the difference between experimental data and refinement data. The vertical bars indicate the MnBi magnetic (first row), MnBi Bragg (second row), and Bi Bragg (third row) peak positions.]

multiple phase refinements as well as magnetic structure refinements of each of the coexisting phases. It is found that there is approximately 90 wt % of LTP MnBi in the magnetically separated powders. The MnBi alloys have the NiAs-type structure with lattice parameters $a=4.2827$ Å and $c=6.1103$ Å, which corresponds to the LTP MnBi.[10,15] Figure 2 shows the temperature dependence of the magnetic moments of the Mn atom and the angle between the moments and the $c$ axis in the MnBi LTP. As shown in Fig. 2, the magnetic moment of the Mn atom shows a small temperature dependence in the range from 10 to 300 K. The magnetic moment per Mn is 3.60 $\mu_B$ and 4.18 $\mu_B$ at room temperature and 10 K, which is well in agreement with the magnetic measurements on polycrystalline MnBi,[4,8] on single crystals,[15] and with theoretical band calculations.[17,18] The value at room temperature (RT) is considerably less than that obtained by previous neutron diffraction measurements,[7] where a value of $4.5\mu_B$ was claimed at RT. Below 200 K, the magnetic moments of Mn deviate gradually from the direction parallel to the $c$ axis and into the direction nearly perpendicular to the $c$ axis at 50 K. A sharp increase of the angle between Mn magnetic moments and the $c$ axis is observed around 90 K. However, the magnetic moment still shows a very small $c$-axis component at 10 K, i.e., it is not totally in the basal plane. Therefore, a canted magnetic structure is formed in MnBi LTP from 200 to 10 K. This is consistent with the suggestion of Roberts,[8] that the magnetic moments do not rotate completely from along the $c$ axis into the basal plane at temperatures below 84 K. However, it is different from other studies which concluded that the magnetic moments flip into the basal plane at 90 K.[2,15,19]

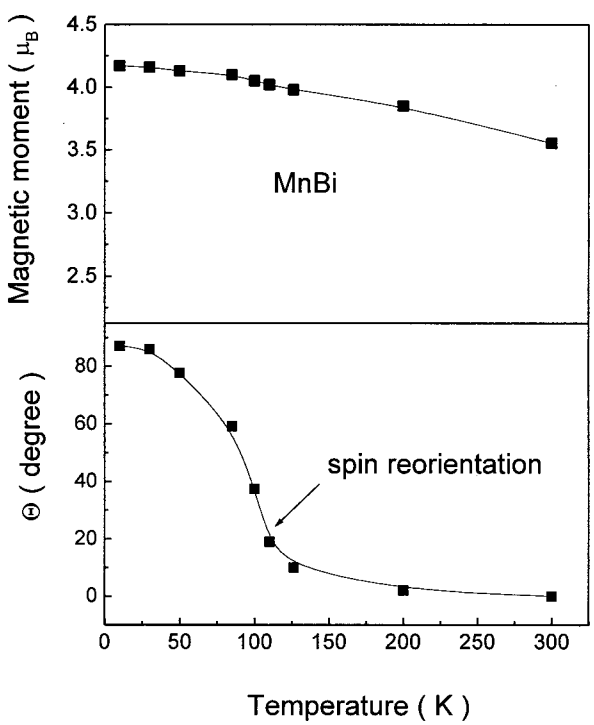


FIG. 2. The temperature dependence of the Mn magnetic moments and the angle between magnetic moments and $c$ axis in MnBi.

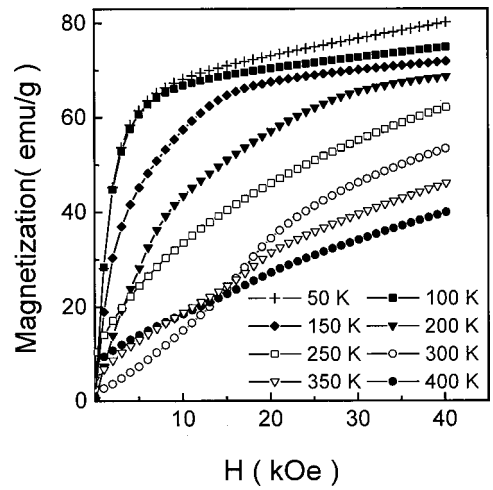


FIG. 3. The magnetization curves along the direction perpendicular to the aligned direction at different temperatures.

The magnetization curves measured perpendicular to the aligned direction are shown in Fig. 3. 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 planar anisotropy below 50 K. This is consistent with our neutron data. Our neutron data show a canted magnetic structure below 200 K, different from the results obtained from the magnetization curves of a LTP single crystal,[15] where a basal-plane anisotropy was observed below 100 K. Coehoorn *et al.*[17] 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–

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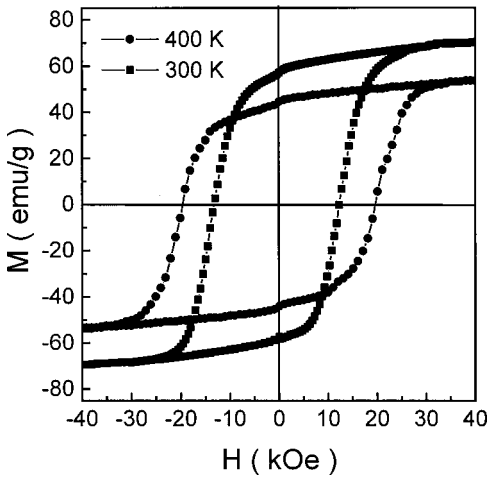


FIG. 4. Hysteresis loops of MnBi magnets at 300 and 400 K.

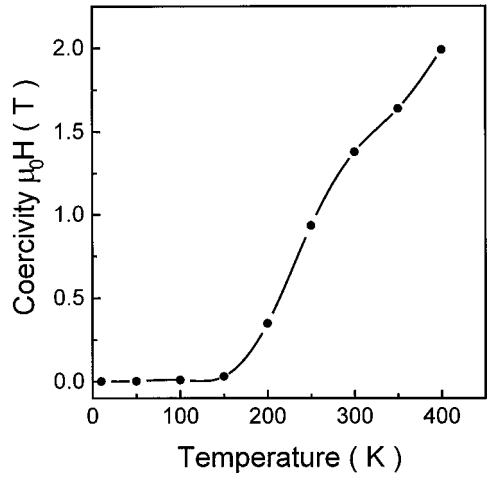


FIG. 5. Dependence of the coercivity on temperature for MnBi magnets.

dipole interaction cannot explain the basal anisotropy at low temperature. Additionally, recent band calculations with spin–orbital coupling and orbital polarization still result in disagreement between theoretical and experimental results.[18] Further studies regarding the temperature dependence of the anisotropy of MnBi are necessary.

The high purity MnBi powders were further ground under the protection of the *n*-heptane for several hours and the fine powders were fixed into an epoxy resin with a magnetic field of about 1.0 T to form aligned samples of cylindrical shape. Figure 4 shows hysteresis loops of resin-bonded MnBi magnets measured at 300 and 400 K. Coercivities of 2.0 and 1.4 T were observed at 400 and 300 K, respectively. The coercivity shows a large temperature dependence. The dependence of the coercivity on the temperature was shown in Fig. 5. 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 reported for samples prepared by melt-spinning,[4] which may be attributed to a different coercivity mechanism. Below 150 K, the coercivity tends to zero due to the anisotropy change. The maximum energy product $BH_{max}$ of the magnet is 7.7 MGOe(61 kJ/m$^3$) and 4.6 MGOe (37 kJ/m$^3$) at room temperature and 400 K are the largest values reported thus far for MnBi magnets. A density of 7.8 g/cm$^3$ for MnBi was used in the calculation of the energy product.

## IV. CONCLUSIONS

High purity LTP MnBi has been synthesized and the structure and magnetic properties of the LTP have been investigated. The 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 37 kJ/m$^3$ has been achieved at 400 K. A sharp increase at about 90 K in the angle between Mn magnetic moment and *c* axis indicated a spin reorientation of MnBi LTP. The anisotropy changes from uniaxial anisotropy at 400 K to the canted below 200 K.

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