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Alignment and analyses of MnBi/Bi nanostructures

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A Mn_5Bi_{95} alloy was rapidly solidified into a mixture of nanocrystalline Bi and metastable Bi(Mn). Heating the ribbons to temperature $T=525$ K in a dc magnetic field causes formation and *c*-axis alignment of low-temperature phase (LTP) MnBi nanorods along the applied field direction. Nanorod alignment increases with increased magnetic field, with a calculated alignment half-angle of 47° for a sample heated to 520 K at 50 kOe. *In situ* magnetization changes suggest that nanorod alignment is achieved by rotation of MnBi particles. Particle alignment enables the measurement of the MnBi nanorod spin reorientation temperature of 100 K, the same as its bulk counterpart. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2008368]

The crystallographic alignment of uniaxial magnetic nanocrystals with respect to their supporting substrate or matrix is an important technological challenge, often with incompletely understood governing forces and conditions. Crystallographic alignment of the easy axis of magnetization is essential to the realization of a high maximum energy product $(BH)_{max}$ in advanced permanent magnets,[1] underlies the design of future high-density perpendicular magnetic and magneto-optic recording media,[2] and facilitates the optimization of ultrasoft magnetic materials.[3]

Because of its high uniaxial magnetic anisotropy ($\sim 2 \times 10^7$ erg/cm^3 at 500 K) along its *c*-axis and record magneto-optical Kerr rotation of 1.25° at room temperature,[4] the low-temperature phase (LTP) of equiatomic MnBi with the hexagonal NiAs structure has received much attention since the 1950s due to potential applications in high-temperature permanent magnets[5] and in data storage.[6] Among other factors, however, the implementation of MnBi in these advanced applications has been limited[7] by typical synthesis methods resulting in rather large coupled grains that cause high media-noise readout[8] and low energy products.[9] Its technological potential notwithstanding, motivation exists to investigate the properties of nanoscaled MnBi as it is anticipated that its magnetic and structural attributes will differ from those observed in its larger-grained forms. Improved control and understanding of the structure-magnetic connections in MnBi may allow its implementation into multifunctional sensors that simultaneously detect thermal and magnetic environment changes, an emerging technology. Recent work done by the present authors builds upon and extends previous research[10–12] that exploits the low-temperature eutectic reaction in the binary Mn-Bi phase diagram at approximately 5%Mn-95%Bi to synthesize a regular two-phase microstructure of MnBi and Bi. The synthesis of isolated LTP MnBi nanorods with average diameter 10 nm and average length 30 nm embedded in a Bi matrix was achieved by rapid solidification of the eutectic composition followed by a moderate annealing treatment.[13] The nanorods are sparsely (~ 7 vol %) but isotropically distributed and, in agreement with related studies,[14,15] possess coercivities on the order of 17 kOe at room temperature and a Curie temperature $T_C=540$ K on heating that is significantly depressed relative to the bulk LTP MnBi Curie temperature 628 K. The high coercivity of the MnBi nanoparticles reported in the current study may attract the interest of the permanent magnet community; work of similar intent was performed by Yelon *et al.*[16] In this letter we report on the easy-axis alignment of the nanoparticles resulting from *in situ* application of a magnetic field during low-temperature annealing. We report on the phenomenon and conditions of field-induced crystallographic texturing of the MnBi nanorods, presenting a method to tailor the alignment of MnBi nanostructures.

Mn-Bi ribbons (4 mm wide $\times$ 40 μm thick, with lengths less than 5 mm) were fabricated from a charge of nominal composition Mn5-Bi95 (at %) by melt-spinning. The sample was induction melted then ejected using 525 Torr compressed Ar gas onto a water-cooled rotating copper wheel (28 m/s) for rapid solidification. X-ray diffraction and plan-view transmission electron microscopy (TEM) reveal that the as-quenched ribbons consist only of polycrystalline Bi. Evidence of LTP MnBi is obtained only after annealing to $\sim$400 K, suggesting that rapid solidification causes the Mn to be metastably retained in the Bi matrix as either a substitutional or an interstitial impurity. The as-quenched ribbons were sealed in silica tubes in a vacuum better than 3×10^{-6} Torr and data was collected in a furnace insert to the superconducting quantum interference device (SQUID) magnetometer cryostat upon heating and cooling in the range $300\ \text{K} \leqslant T \leqslant 525$ K in the presence of a selection of dc magnetic fields $H \leqslant 50$ kOe. Additionally, ac and dc susceptibility measurements were made on the aligned samples in the range $5\ \text{K} \leqslant T \leqslant 300$ K. The temperature dependence of the ac magnetic susceptibility χ_{ac} was measured with a zero dc bias field and ac field of 2.0 Oe at a frequency of 300 Hz. The low-temperature dc magnetic moment was investigated with fields $\leqslant 10$ Oe. No corrections to the data were made for demagnetization effects. Ribbon pieces were mounted with their flat surfaces perpendicular to the direction of the applied field in the silica tube and care was taken to maintain this alignment for subsequent x-ray diffraction studies. The heating and cooling rates were controlled to 2.5 K/min.

Typical demagnetization curves measured at 300 K for ribbons heated to 520 K in applied fields of 0 kOe, 10 kOe, and 50 kOe are presented in Fig. 1. The temperature of 520 K was chosen because it is below the Bi melting temperature of 545 K but is well above the nucleation temperature ($\sim$400 K) of the LTP MnBi nanoparticles in the as-

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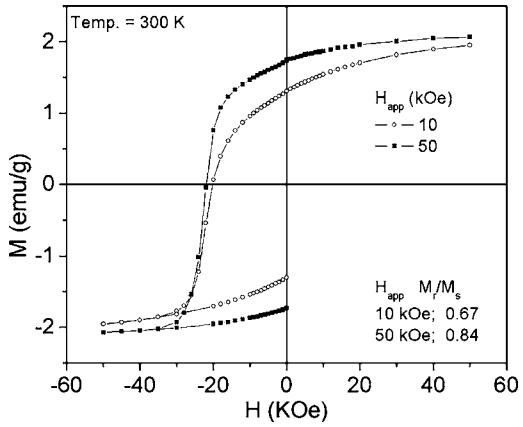

FIG. 1. 300 K demagnetization curves for samples heated to 520 K in 10 and 50 kOe fields.

quenched ribbons. Because previous studies indicate that the uniaxial MnBi nanorods are well-separated and single-domain,[13] it is a simple exercise to use the remanence to calculate the degree of particle alignment. Ribbons heated in the zero-field condition reveal a remanence ratio M_r/M_s of 0.5, where M_r is the remanence and M_s is the saturation magnetization. This result is in agreement with that expected from a ferromagnetic material composed of randomly-oriented uniaxial single-domain particles.[17] Determination of the orientation of the particle ensemble is obtained by a calculation of the distribution cone angle corresponding to a measured remanence as follows. Let α be the angle of largest deviation of the easy magnetization axis from the direction of the previously applied magnetic field direction. At remanence the particle magnetization lies within a cone of half-angle α in the positive direction and the distribution covers a portion of a corresponding positive hemisphere. The remanence is given by

$$M_r = \int_0^{\alpha} M_s \left(\int_0^{\alpha} \sin\alpha \, d\alpha \right)^{-1} \sin\alpha \cos\alpha \, d\alpha. \qquad (1)$$

An isotropic particle distribution is represented by $\alpha = 90°$, with $M_r/M_s = 0.5$. Ribbons heated to 520 K in an applied field of 10 kOe yield $M_r/M_s = 0.67$, indicating partial alignment of particles' c-axes along the field direction with a cone half-angle $\alpha \approx 70°$. When the same heating process is applied to an as-quenched sample under a higher field of 50 kOe, a remanence ratio M_r/M_s of 0.84 was observed, consistent with an alignment cone half-angle of $\alpha \approx 47°$. Simple extrapolation of the trend of applied field versus remanence ratio M_r/M_s suggests that a field of ~80 kOe applied at a maximum temperature of 520 K should result in close to 100% nanoparticle alignment, $M_r/M_s = 1$ or $\alpha = 0°$.

Demagnetization curves measured at 300 K for samples heated to the maximum temperatures T_{max} of 510, 520 or 525 K are presented in Fig. 2(a). The curves for the samples with the $T_{max} = 510$ and 520 K overlap with $M_r/M_s = 0.67$. In contrast, the sample with $T_{max} = 525$ K exhibits a remanence ratio $M_r/M_s \sim 1.0$, consistent with nominally complete alignment of the MnBi nanorods along the direction of the applied field. These results underscore the importance of heating temperature for tailoring the alignment degree of MnBi nanocomposites, in agreement with results obtained on coarse-grained MnBi composites by Ren *et al.*[18] To clarify the alignment mechanism, the magnetization signal was re-

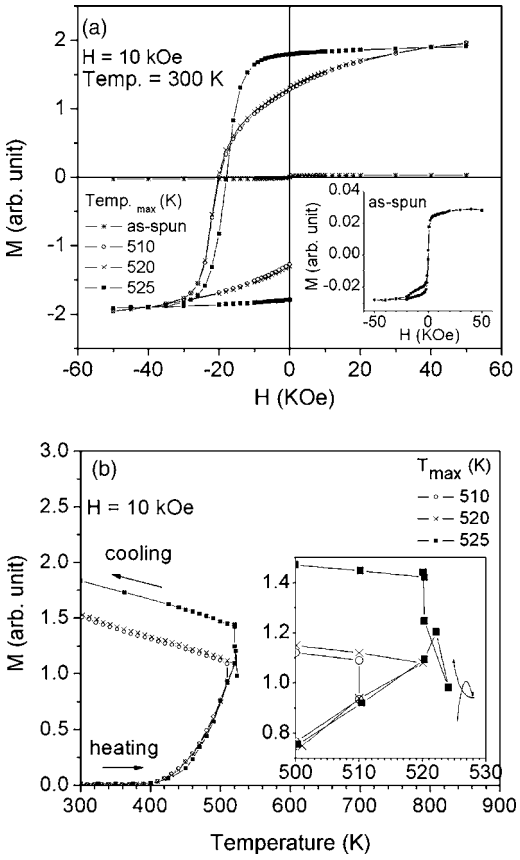

FIG. 2. (a) 300 K demagnetization curves for samples as-spun and heated to 510, 520, and 525 K in 10 kOe; (b) M-T curve in 10 kOe measured upon heating and cooling. The inset is an enlarged M-T curve in range 500 K $\leqslant T \leqslant$ 530 K.

corded upon heating and cooling in a 10 kOe magnetic field, Fig. 2(b). In comparison with samples with $T_{max} = 510$ and 520 K, the sample heated to 525 K shows a more complex change in the magnetization trends: the magnetization exhibits an abrupt drop at 525 K [inset Fig. 2(b)] followed by a significant increase in the moment upon cooling, greater than that produced by excursions to the lower temperatures. The decreased magnetization above 525 K is attributed to the first-order phase transformation from LTP MnBi to the high-temperature-phase (HTP) form of MnBi. In this phase the bipyramidal interstices of the NiAs structure are stuffed with Mn cations to a nominal composition of $Mn_{1.08}Bi$ with the distorted Ni_2In structure, creating a paramagnetic or an antiferromagnetic state.[19,20] A room-temperature hysteresis curve measurement of the 525 K-heated sample yields a remanence ratio of unity, Fig. 2(a).

The nanorod alignment is confirmed by room-temperature Cu K_α x-ray diffraction spectra measured on ribbons in their as-spun state and annealed in zero-field or 10 kOe, Fig. 3. The zero-field-annealed sample's Bragg peak intensities are consistent with those of bulk MnBi, and thus no appreciable preferred orientation is produced. However, the sample heated in a 10 kOe field shows a stronger LTP MnBi (002) peak, consistent with c-axis preferred orientation of particles aligned perpendicular to the ribbon surface and parallel to the applied field.

Other researchers have observed alignment of MnBi in the presence of a magnetic field and have proposed two mechanisms for MnBi alignment: recrystallization and crystallite rotation. Chen and Stutius[21] report that heating a MnBi

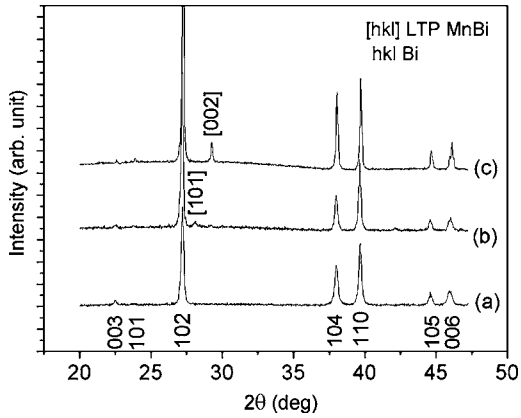

FIG. 3. X-ray spectra for samples (a) in as-spun state and (b) heated in zero-field, and (c) 10 kOe field conditions.

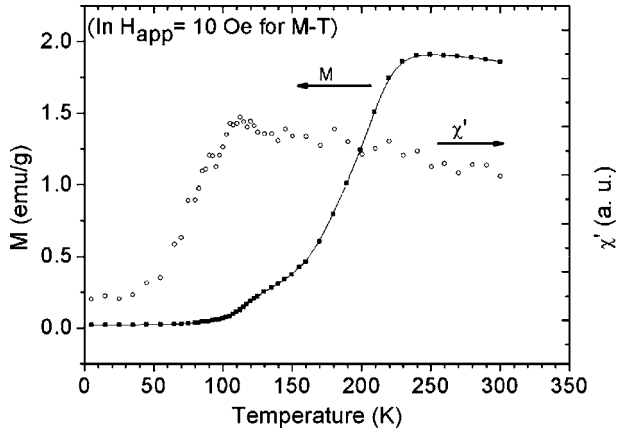

FIG. 4. dc *M-T* curve measured at 10 Oe and the real component χ' of the ac-susceptibility χ_{ac} for a sample with aligned MnBi particles oriented along the applied field direction.

single crystal in a magnetic field (15–20 kOe) oriented perpendicular to the easy magnetization *c*-axis of the crystal causes the crystal to subdivide and recrystallize with an orientation parallel to the field. It should be noted that a relatively high heating temperature of 603 K and a very long annealing time (2500 min) are required in that study for recrystallization. In contrast, in the present study complete particle alignment was achieved in the present study within 60 s at the lower temperature of 525 K. On the other hand, Ren *et al.*[18] reported the alignment of coarse MnBi crystallites in MnBi-Bi eutectic rods in 30 min under the action of a 10 kOe magnetic field at 573 K. Employing metallographic analyses, they estimated a crystallite deviation angle of 15° from the direction of the applied magnetic field and hypothesized that a rotation of the crystallites was driven by magnetostatic forces balanced by frictional forces of the semisolid matrix. It is therefore reasonable to suggest that the abrupt *c*-axis reorientation of the MnBi nanorods observed in our sample upon cooling from 525 to 520 K arises from particle rotation along the applied magnetic field direction.

In addition to exhibiting a remanence ratio approaching unity, samples with aligned MnBi nanorods allow effective study of the spin reorientation, which is reported to be in the vicinity of 90–100 K in bulk MnBi samples.[22–24] It was not possible to definitively ascertain the spin reorientation temperature in the isotropic MnBi-Bi nanocomposite due to the broadness of the transition.[13] Ac susceptibility χ_{ac} data from the aligned sample shown in Fig. 4 reveals a bump in the real component χ' at $T \sim 100$ K which is attributed to the spin reorientation from along the *c*-axis toward the *ab*-plane with cooling. The corresponding dc magnetization *M* measured in a 10 Oe field decreases gradually with decreasing temperature from $T \sim 250$ K and shows no further change as the temperature decreases below ~ 100 K. These data indicate that the spin reorientation temperature in nanoscaled MnBi does not differ from its bulk value. In contrast, the Curie temperature of this nanocomposite was found to be depressed by 140 K from the reported bulk value.[13] However, Yoshida *et al.*[23] did record a marked increase in the MnBi spin reorientation temperature with increased pressure. Thus the origin of the decreased Curie temperature in these macrostructure samples is not yet clear.

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