Anomalous magneto-structural behavior of MnBi explained: a path towards an improved permanent magnet

N.A. Zarkevich,1 L.-L. Wang,1 and D.D. Johnson1,2
1) The Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011 USA
2) Materials Science and Engineering, Iowa State University, Ames, Iowa 50011 USA

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Low-temperature MnBi (hexagonal NiAs phase) exhibits anomalies in the lattice constants (a, c) and bulk elastic modulus (B) below 100 K, spin reorientation and magnetic susceptibility maximum near 90 K, and, importantly for high-temperature magnetic applications, an increasing coercivity (unique to MnBi) above 180 K. We calculate the total energy and magneto-anisotropy energy (MAE) versus (a, c) using DFT+U methods. We reproduce and explain all the above anomalies. We predict that coercivity and MAE increase due to increasing a, suggesting means to improve MnBi permanent magnets.

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MnBi in its low-temperature phase (LTP) has one of the most extraordinary magnetic properties among ferromagnetic materials.22–24 Uniquely, its coercivity increases with temperature (T), and its value is larger than that of Nd2Fe14B above 423 K, making it potentially an excellent permanent magnet for high-temperature applications. MnBi does not contain critical rare-earth elements and, thus, it has a potential for technological impact. If magnetic anisotropy energy (MAE) is better controlled and tuned, use of MnBi magnets could be broadened. Below we provide theoretical explanation for the long-standing experimental puzzles in the measured coercivity, spin orientation, and bulk modulus of MnBi. We also suggest a means to further increase the MAE.

Despite its simple NiAs hexagonal structure (Fig. 1), MnBi exhibits several puzzling behaviors versus T. First, the lattice constant a exhibits minimal thermal expansion below 70 K and then expands rapidly during the spin reorientation, while c shows a chaotic zigzag behavior below 150 K. Second, there is a measured kink in the bulk modulus (B) near 39 GPa at 100 K. Third, a spin reorientation is observed at TS_R ≈ 90 K when the magnetization M(T) easy axis changes from in-plane to c-axis above TS_R. Next, coercivity is near zero at T < 180 K, and increases with T above 180 K. Finally, above 628 K MnBi transforms to a high-T oP10 phase (stable between 613 K and 719 K) with M=0.1

We explain all these observations by examining dependence of the calculated total energy (E) and MAE on the lattice geometry (Figs. 2, 3, 4, and 5). The total energy is anisotropic versus (a, c), like a “flat-bottom canoe,” and its asymmetry causes abnormal thermal expansion. Due to the nature of the potential energy surface, the second derivative of the total energy with respect to volume is not monotonic, producing a kink in B= V d²E/dV² near 39 GPa, whose origin can be traced to features in electronic density of states (DOS). Spin reorientation arises from a change of sign in MAE, which depends on increasing a. This suggests simple means to control MAE: by thermal expansion (observed), or by strain or alloying, e.g., coherent interfacing or doping. While temperature and strain affect mostly (a, c), doping can induce competing effects on MAE, some of which can be beneficial. Preliminary results suggest that doping with selected metals (Ni, Rh, Pd, Ir) increases MAE and coercivity and stabilize the spin orientation along c at all temperatures.

Computational method: We use a DFT+U method implemented in the Vienna ab initio simulation package (VASP). We use 16 × 16 × 10 Monkhorst-Pack k-point grid with the Γ-point, a 337 eV plane-wave energy cutoff and 500 eV augmentation charge cutoff, for both energy and magnetic anisotropy energy. A modified Broyden’s method is used for electronic self-consistency. Bulk moduli are found from dependence of the total energy E(a, c) on volume V = ca²√3/2. MAE is the energy difference with moments along (1210) and then (0001), i.e., E[1210]−E[0001]. Generally, the MAE can be the order of μeV to meV; in MnBi for changes in a, pertinent to thermal lattice expansion effects, changes

FIG. 1: MnBi hexagonal structure (hP4, P63/mmc, No.194), with 0.0323 e/Å³ charge density isosurfaces. (0001) projection (left), and primitive unit cell (right) with two Mn (red) and two Bi (green) atoms.

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1) Electronic mail: zarkev@ameslab.gov
are order of meV. We improve description of the electronic structure (and, hence, magnetization and lattice parameters) by combining the spin-polarized, generalized gradient approximation (GGA)\textsuperscript{29} with the rotationally invariant DFT+U formalism.\textsuperscript{27} GGA includes local value and gradient of the electron density $n = n_t + n_s$ and spin density $n_s \quad (\sigma = \uparrow, \downarrow)$ in the exchange-correlation functional $\varphi_{\text{GGA}} = E_{\text{GGA}}[n_t, n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}]$.\textsuperscript{28} DFT+U corrects the total energy\textsuperscript{29} for presence of localized states, i.e., $E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{1}{2} (U - J) + \sum_{\sigma} n \cdot n_{\sigma} = \varphi_{\text{DFT}}[n_t, n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}]$.\textsuperscript{28} DT+U is necessary to improve description of the electronic structure and to better reproduce the measured lattice constants, volume, and magnetic susceptibility.\textsuperscript{125} The calculated lattice constants, volume, and magnetization are in quantitative agreement with experiment,\textsuperscript{121,122} although changes of $\varphi$ coefficients ($\alpha = \varphi / \varphi_0 \approx -\frac{1}{2} N k_0 c_s^2$) is $1.15 \cdot 10^{-5}$ K$^{-1}$, in agreement with experiment\textsuperscript{123} i.e., $1.168 \cdot 10^{-5}$ K$^{-1}$. Hence, the potential energy surface in Fig. 2 predicts no thermal expansion along $a$ at low $T < 70$ K, and a positive expansion at higher $T$ above 100 K, as observed.\textsuperscript{12} The spin reorientation in MnBi near 90 K was not fully understood in experiments.\textsuperscript{11,12} Moreover, previous DFT calculations of MAE found the easy axis to be always in-plane (Table 3 in Ref. 121). We calculate dependence of the MAE on ($a$, $c$), and find that it is strongly affected by $a$ and very weakly by $c$, see Fig. 2. Thus, thermal expansion of $a$ causes the MAE to change from negative (in-plane oriented moments) to positive (moments oriented along the $c$-axis). This sign change causes a spin reorientation, experimentally observed around 90 K\textsuperscript{11,12} Magnetic susceptibility has maximum at $\text{MAE}=0\textsuperscript{11,12}$ when spins easily reorient along the external applied magnetic field. Coercivity is zero if $\text{MAE} < kT$, but increases with MAE at $T > 180$ K\textsuperscript{12}. Thus, dependence of MAE on ($a$, $c$) causes spin reorientation and explains the thermal behavior of magnetic susceptibility and coercivity.

Another consequence of the anomalous potential energy surface $E(a, c)$ is the observed kink in B near 39

| $a$ ($\text{Å}$) | $c$ ($\text{Å}$) | $c/a$ | $V$ ($\text{Å}^3$) | $\mu_B$ | Ref. |
|---|---|---|---|---|---|
| 4.286 | 6.126 | 1.428 | 94.928 | 3.54 | GGA |
| 4.286 | 6.126 | 1.428 | 94.928 | 3.54 | GGA |
| 4.28 | 6.11 | 1.427 | 95.936 | 3.54 | GGA |
| 4.305 | 5.718 | 1.380 | 86.656 | 4.50 | GGA+U |
| 4.26 | 6.05 | 1.420 | 95.083 | 3.7 | ASM |
| 4.30 | 6.12 | 1.423 | 97.998 | 3.50 | LCAO |

$^a$ Note: $a$ and $c$ were fixed in Refs. 35 and 36.
FIG. 2: Change in the total energy $E$ at 0 K vs. $(\Delta a, \Delta c)$, with 3 meV/cell (or 34.8 K) between contours. Constant volume ($ca^2\sqrt{3}/2$) is the line through (0,0).

FIG. 3: $E(\Delta a, \Delta c = 0)$. GGA+U results (circles) with cubic (line) and quadratic (dashed) fits, and their difference $\Delta E$ (black line, right scale). $h\omega = 7.7$ meV (90 K) is the horizontal dotted line in the inset.

FIG. 4: MAE vs. $(a, c)$ with 0.1 meV/cell steps in contours from zero (grey line). Assessed data (circles) is shifted by 0.83% (filled circles), see text.

FIG. 5: $B$ vs. $a$ at isotropic expansion ($a/a_0 = c/c_0$) relative to $a_0 = 4.2827\AA$ and $c_0 = 6.1103\AA$. (Inset) Spin DOS (states/[cell·eV]) for 3 values of $a/a_0$.

GPa at 100 K, a long-standing puzzle. We calculate $B = Vd^2E/dV^2$ from dependence of $E(a,c)$ on $V = ca^2\sqrt{3}/2$ at isotropic expansion ($\Delta a = \Delta c$ in Fig. 2). We find that $B$ versus $a$ (Fig. 5) is not monotonic near $B = 39$ GPa, as observed. This kink originates from a change in DOS at the Fermi level (Fig. 5; see also Fig. 4 in Ref. 34). The Fermi level ($E_F$) is in a pseudo-gap, and the minimum in the minority-spin DOS passes through $E_F$ with thermal expansion of $a$; the DOS minimum corresponds to the $a$ at $B=39$ GPa (inset, Fig. 5).

Summary: We calculated dependence of the total energy and magneto-anisotropy energy on the lattice geometry for MnBi low-T phase. Our results explain the unusual structural and magnetic properties, heretofore unexplained. From the potential energy surface, we reproduced and explained the observed anomalous behavior of (i) the lattice constants and (ii) bulk modulus. The calculated MAE changes sign with a small increase in $a$, which causes spin reorientation during thermal expansion. (iii) The magnetic susceptibility has a maximum at MAE=0 (at spin reorientation). (iv) Further increase of MAE with thermally expanding $a$ increases coercivity at $T > 180$ K, where $|MAE| > kT$.

Due to its sensitivity on $a$, the MAE can be altered by temperature, pressure, doping, or interfacial strain. To test whether doping can achieve a positive MAE at all temperatures, we performed preliminary, small-cell calculations that find that doping with selected (Ni, Rh, Pd, Ir) metals increases coercivity and stabilizes the spin orientation along $c$. More extensive calculations for $<3\%$ cationic or anionic doped (substitutions and interstitials) cases are planned to establish the effects on lattice, magnetism, and stability. Our understanding of the anomalous magneto-structural behavior offers an opportunity to develop improved MnBi-based permanent magnets.
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