MAGNETIC ANISOTROPY IN MnBi PARTICLES GROWN BY DIRECTIONAL SOLIDIFICATION OF THE Mn-Bi EUTECTIC

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ABSTRACT

Directional solidification of the eutectic Mn-Bi alloy (2 at% Mn) produces an aligned array of ferromagnetic Mn-Bi needles, 0.1 to 1.5 μm in diameter, in a matrix of diamagnetic Bi. Samples grown at about 50 cm/hr and then annealed at 200°C contain two magnetic phases. One phase is normal equilibrium MnBi, known in the recent literature as the low-temperature phase (LTP). The second phase is crystallographically similar to the high-temperature phase (HTP) $Mn_{1.08}Bi$, but has a much lower Curie temperature of 240 K. Low-temperature hysteresis loops measured parallel and perpendicular to the axis of freezing are of unusual form. If the magnetization due to the normal MnBi phase is subtracted, the resulting loop in the parallel direction has H_{ci} > 100 kOe, suggesting single-domain behavior. The resulting loop in the perpendicular direction can be accounted for by the presence of a relatively large fourth-order anisotropy.

SAMPLE PREPARATION

The preparation of the samples and the measuring techniques have been described in other publications[1-4], and will be very briefly summarized here. Alloys containing 2 at% Mn and Bi, directionally solidified in a temperature gradient, have a structure of long parallel rods, generally 0.5 to 1.5 μm in diameter and of varying cross-sectional shape, in a matrix of Bi. According to the phase diagram [5], the rods should be ferromagnetic MnBi. The volume fraction of MnBi in the samples should be about 3%, and the magnetization per gram of sample should be about 2 emu/g. Samples frozen at low growth rates (1-10 cm/hr) have magnetic properties consistent with this prediction, but samples frozen at a faster rate show more complicated magnetic behavior. Results on these samples show less scatter after annealing for 15 min to 48 hrs at 200°C; this may be due to relaxation of stresses caused by differential thermal contraction of the particles and the matrix.

MAGNETIC PROPERTIES

Below about 240K, there is clear evidence for two magnetic phases. One phase is the expected equilibrium MnBi, generally known as the low-temperature phase (LTP). The other phase has the symmetry and lattice parameters of the phase $Mn_{1.08}Bi$, stable only above 340°C and known as the high-temperature phase (HTP) or, when retained below 340°C by rapid cooling, as the quenched high-temperature phase (QHTP)[5,6]. However, QHTP has a Curie temperature of 450 K and the phase in our samples has a Curie temperature of about 240 K.

Measured hysteresis loops parallel and perpendicular to the axis of freezing are shown in Fig. 1. The jumps in magnetization near H=0 at low temperatures are attributed to the LTP MnBi, which has low anisotropy and low coercive field at low temperatures. The two magnetic phases appear to be independent, so that the magnetic properties of the sample are simply the sum of the magnetic properties of the two phases. The magnetization of the LTP MnBi can then be subtracted from the measured loops by assuming the LTP contribution is a perfectly square loop with small H_{ci}. The resulting loops are shown in Fig. 2.

The $\sigma_{\parallel}$ loops are essentially rectangular, with H_{ci} about 100 kOe. At temperatures below about 100K, the measured H_{ci} is limited by our maximum field of 125 kOe. The measurements of Chen and Stutius[6] on a bulk

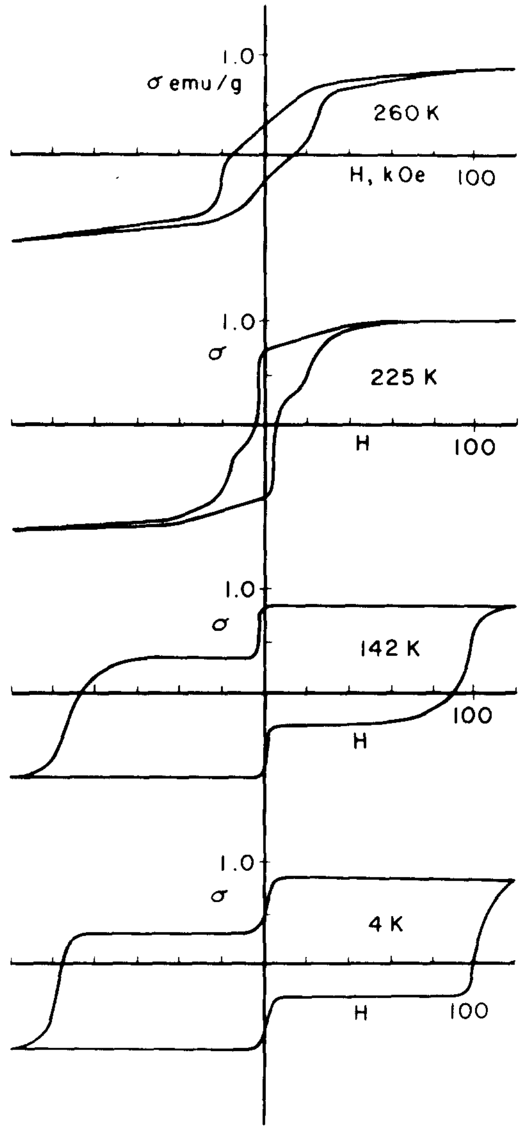

Fig. 1a. Measured hysteresis loops parallel to the freezing axis. Magnetization is given in moment per gram of sample (MnBi plus Bi).

single crystal of QHTP give (at low temperature) $K_u = 4\times10^7$ erg/cm^3 and M_s = 600 emu/cm^3, corresponding to an anisotropy field $2K_u/M_s$ of about 130 kOe. It appears that the particles are behaving as ideal Stoner-Wohlfarth single-domain particles with $H_{ci} = H_k$.

For a simple uniaxial anisotropy, the $\sigma_{\perp}$ loop should be a straight line through the origin, reaching the saturation magnetization σ_s at $H = H_k$. Our measured loop is very different (Fig. 2). The moment remains low to a field approximately equal to H_{ci} measured for $\sigma_{\parallel}$, and then rises sharply to saturation. In decreasing fields, the moment drops back to a low value in a large positive field. This drop in moment in a positive field suggests some kind of spin-flip or metamagnetic transition, but there is no evidence for such a transition in the $\sigma_{\parallel}$ loop.

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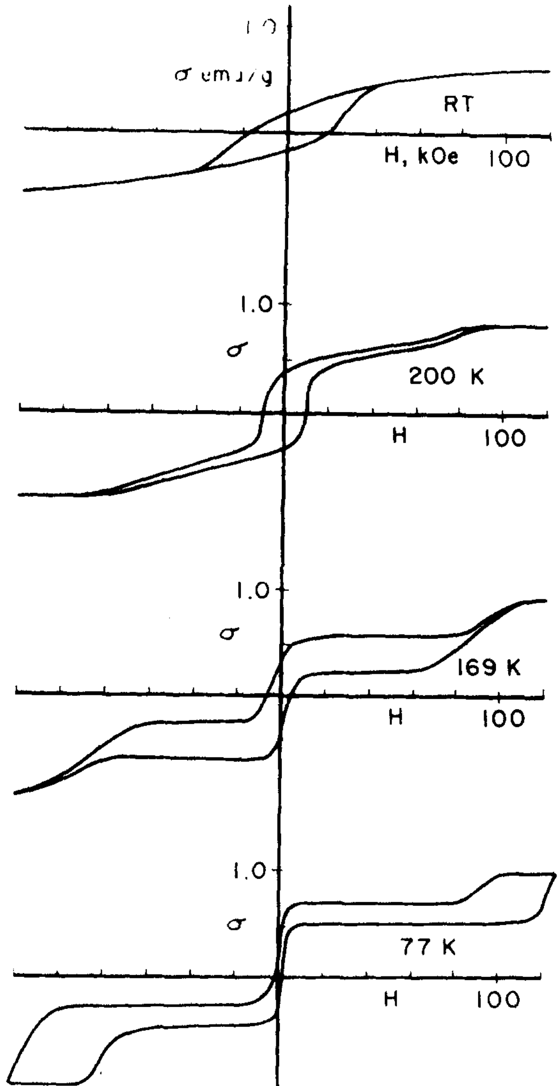

Fig. 1b. Same as 1a, measured hysteresis loops perpendicular to the freezing axis.

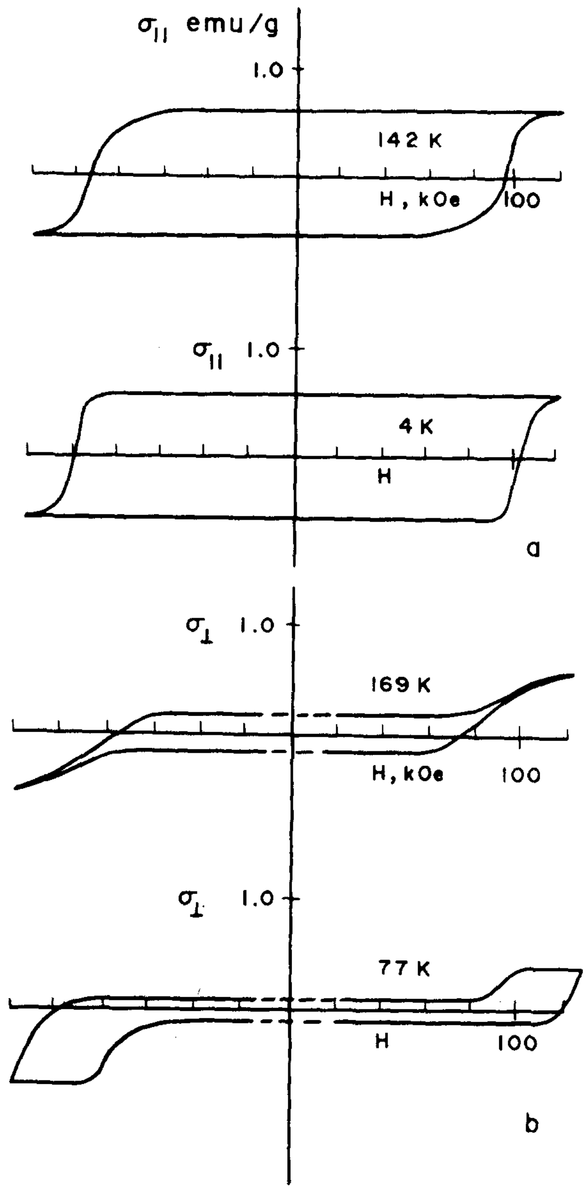

Fig. 2a and b. Low-temperature hysteresis loops of Fig. 1, with magnetization of equilibrium MnBi subtracted.

If we idealize the measured loop as shown in Fig. 3a, we can define two coercive fields H_{c2} and H_{c3}. The temperature dependence of these fields is indicated in Fig. 3b.

DISCUSSION

We suggest that the behavior of $\sigma_\perp$ is qualitatively consistent with rotation of the moment against a crystal anisotropy having a significant fourth-order contribution. We express the anisotropy in a series of spherical harmonics:

$$E_k = k_2[(\tfrac{1}{2}(3\cos^2\theta-1)] + k_4[\tfrac{1}{8}(35\cos^4\theta-30\cos^2\theta + 3)]+ \dots$$

Hysteresis loops parallel and perpendicular to the anisotropy axis can then be calculated [7] for any combination of k_2 and k_4. Similar calculations have been made by Miller and Igarashi[8] and by Melville et al.[9] For the range $0.1 < k_4/k_2 < 0.4$, the predicted loops are similar to those of Fig. 3; Fig. 4 shows the calculated loops for $k_4/k_2 = 0.24$, and the agreement with experiment is qualitatively satisfactory.

The upward and downward jumps in magnetization in the $\sigma_\perp$ loops are the most prominent features of the measured and of the calculated curves. Experimental values of H_{c2} and H_{c3} from Fig. 3a can be used to deduce the values of k_2 and k_4 as a function of temperature, assuming M_s is independent of temperature and equal to 600 emu/cm^3; the results are shown in Fig. 5. The values at 100K are -3×10^7 and 6.5×10^6 erg/cm^3, corresponding to $K_u = 2.3\times10^7$. This is not unreasonable in comparison with the Chen and Stutius [6] value of 4×10^7, especially in view of the great difference in T_c between our phase and the QHTP.

SUMMARY

The aligned eutectic of MnBi in Bi appears to be a good experimental approximation to the ideal assembly of single-domain Stoner-Wohlfarth particles. The behavior of our samples is consistent with the presence of two kinds of MnBi particles, one of equilibrium MnBi and the other of a phase with symmetry and lattice parameters similar to $Mn_{1.08}Bi$ (QHTP), but with much lower Curie temperature and with substantial fourth-order as well as second-order anisotropy at low temperatures.

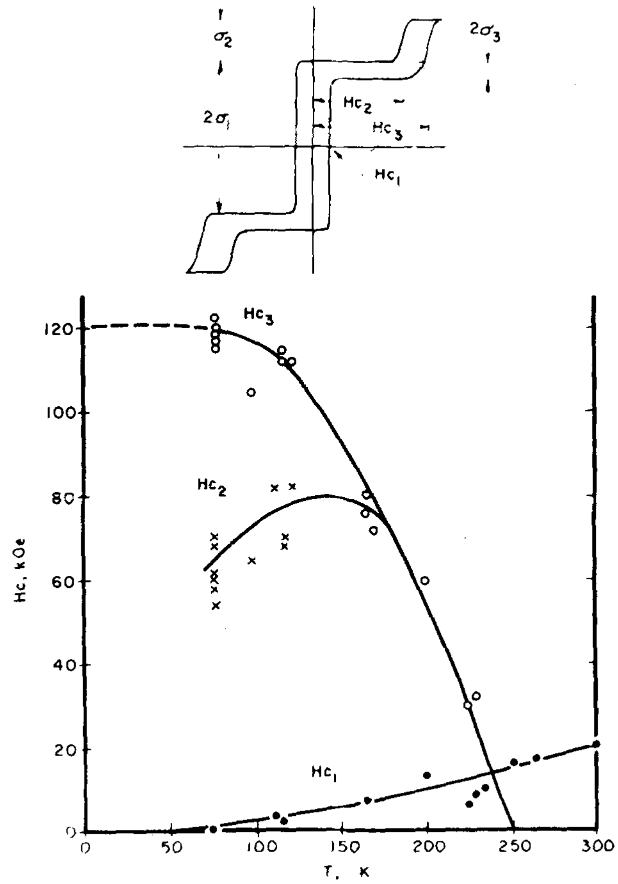

Fig. 3a. Idealized hysteresis loop $\sigma_{\perp}$, defining H_{c1}, H_{c2}, and H_{c3}.
3b. Temperature dependence of coercive fields.

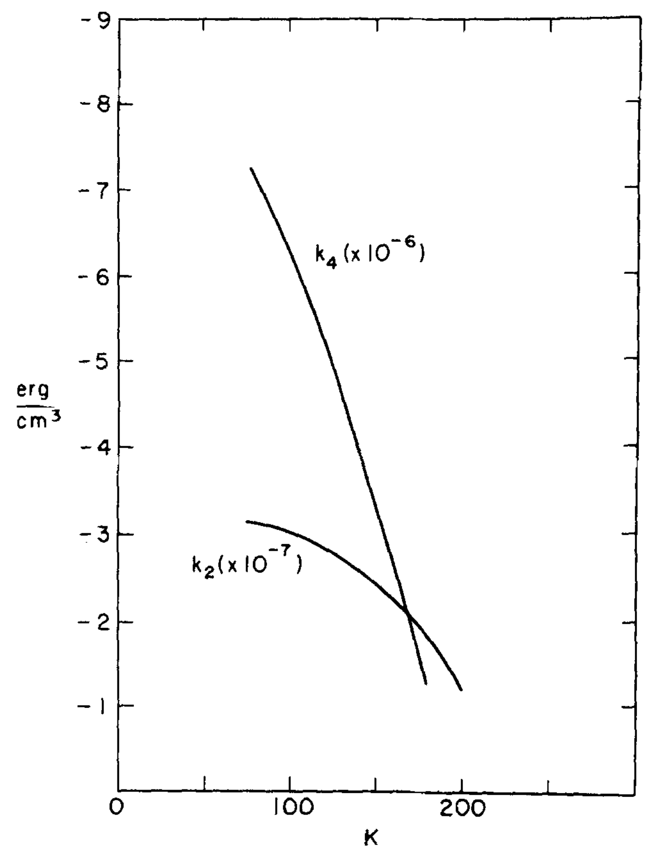

Fig. 5. Temperature dependence of k_2 and k_4 deduced from data of Fig. 3b. Negative k means easy axis at $\theta = 0$.

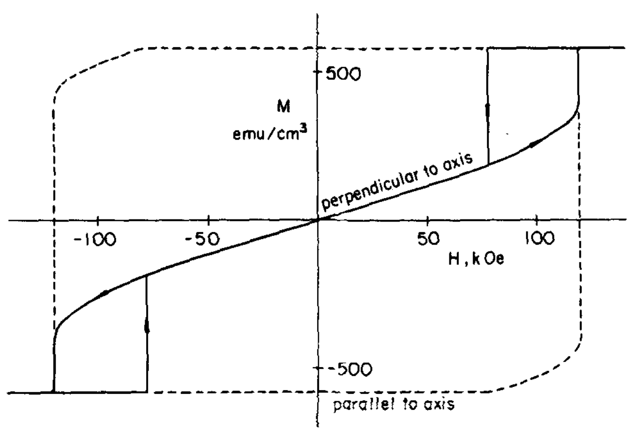

Fig. 4. Calculated parallel and perpendicular hysteresis loops for $k_4/k_2 = 0.24$.

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