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Nuclear magnetic resonance studies of MnSb multi-layered films

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Abstract. ^{55}Mn and ^{121}Sb spin-echo NMR measurements have been carried out at liquid-He temperature on MnSb/Sb multi-layered films. The MnSb layers were shown to grow epitaxially with the *c* axis perpendicular to the film plane. The hyperfine tensors and the anisotropy fields were deduced from the variations in the resonance frequency and linewidth under a DC magnetic field along the *c* axis.

1. Introduction

Recently Nakayama and Shinjo (1988) have succeeded in preparing MnSb/Sb superlattice films by using an ultra-high-vacuum evaporation method. The ferromagnetic MnSb layers were shown by x-ray diffraction to be perpendicular to the [00.1] direction. The MnSb compound is known to have a high Curie temperature (314 °C) and high magnetisation of $4\pi M = 9.5$ kOe. Since MnSb has a hexagonal NiAs-type structure, both Mn and Sb sites have trigonal symmetry and consequently their hyperfine interaction is necessarily anisotropic. However, for the magnetisation lying in the *c* plane the hyperfine field is expected to be isotropic. In this paper we report ^{55}Mn and ^{121}Sb NMR studies on MnSb/Sb multi-layered films in connection with their effective uniaxial magnetic anisotropy. The hyperfine tensors were determined using the same method as for the HCP cobalt thin films (Le Dang *et al* 1986).

2. Experimental procedure

The film samples were grown on Kapton polyimide substrates by alternately depositing Mn and Sb layers using two electron beam evaporators in an ultra-high vacuum (10^{-9} Torr). The thickness of the Sb sublayers was an order of magnitude greater than that of the Mn. The thickness of each layer was monitored with a quartz oscillator. When the substrate was kept at room temperature during the deposition, MnSb layers grew epitaxially in between Sb layers. More details have already been published (Nakayama and Shinjo 1988).

The NMR measurements were carried out at liquid-He temperature using a frequency-variable spin-echo apparatus, with the RF field parallel to the film plane and perpendicular to a DC magnetic field up to 12 kOe. The multi-layered films are designated

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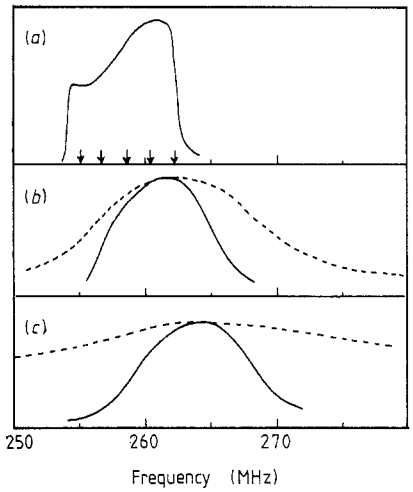

Figure 1. ^{55}Mn spin-echo spectra at 4 K for MnSb films after annealing at 150 °C: ———, normalised results before annealing; ↑, quadrupole splitting observed by Bouwma and Haas for their powder sample at 4 K. (*a*) powder sample; (*b*) t_{Mn} = 12 Å; (*c*), t_{Mn} = 2 Å.

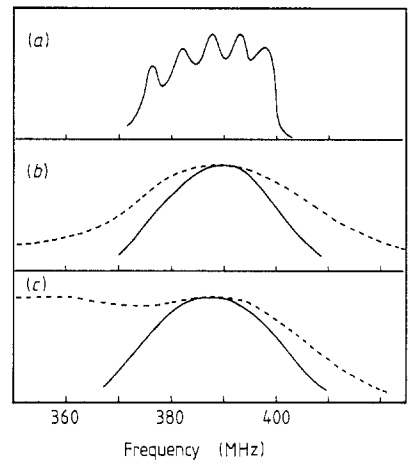

Figure 2. ^{121}Sb spin-echo spectra at 4 K for MnSb films and a powder sample: ———, normalised results before annealing. (*a*), powder sample; (*b*) t_{Mn} = 12 Å; (*c*), t_{Mn} = 2Å.

by $(t_{Sb}, t_{Mn})^n$ with t as the thickness in ångströms of each Sb and Mn layer, where n is the number of repetitions. Two samples $(120, 12)^{27}$ and $(50, 2)^{90}$, deposited on an Sb buffer layer of 600 Å and 700 Å, respectively, were used for the NMR investigations.

3. Experimental results

Torque measurements at 77 K on oriented MnSb single crystals have shown that the first-order anisotropy constant K_1 is strongly negative whereas the second-order anisotropy constant K_2 is positive and one order of magnitude smaller (Okita and Makino 1968). Thus at low temperatures the magnetisation M lies in the c plane. For the film samples with the c axis perpendicular to the film plane the negative anisotropy field is reinforced by the demagnetising field $4\pi M$.

The ^{55}Mn and ^{121}Sb resonance spectra at 4 K in zero external field for the as-prepared samples are much broader (figures 1 and 2) than the total quadrupole splittings for a powder sample of 7 MHz (Bouwma and Haas 1973) and 22 MHz, respectively. These spectra represent the hyperfine interaction when the magnetisation M is *perpendicular* to the c axis. The important linewidth of the film samples arises probably from some off-stoichiometry and interface roughness. In order to improve the crystallisation of MnSb layers we annealed them at 150 °C under a vacuum of 10^{-3} Torr. The x-ray diffraction patterns indicate, for the sample with t_{Mn} = 2 Å, the formation of MnSb clusters with the c axis perpendicular to the film plane. The Mn quadrupole coupling deduced from the spin-echo amplitude modulation (Abe *et al* 1966) is close to that observed for the powder sample. Since the echo amplitude is proportional to the square resonance frequency the Sb satellite lines arising from nuclei at the interfaces are too small to be observed. Such satellite lines would be observable if the symmetry was cubic, giving rise to ^{55}Mn, ^{123}Sb and ^{121}Sb sharp resonance lines.

By applying a DC magnetic field of 12 kOe in the film plane, we measured the sign of the hyperfine fields. It is negative for Mn nuclei as the principal contribution is expected

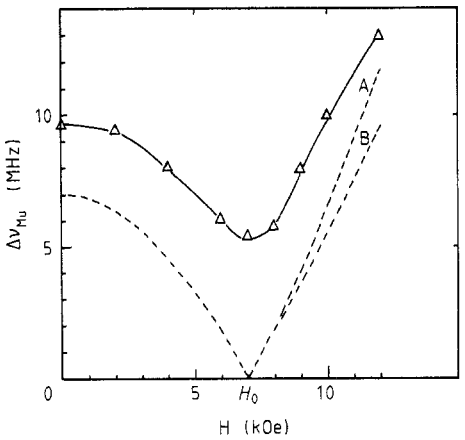

Figure 3. Variation in the Mn linewidth at half-maximum as a function of a DC magnetic field applied perpendicular to the film plane with t_{Mn} = 2 Å (cluster sample): ———, theoretical variation in the total quadrupole splitting with ν_Q = 14 MHz: A, H_{A2} = 1 kOe; B, H_{A2} = 3 kOe.

to arise from the core polarisation. The Sb transferred hyperfine field was found to be positive. To determine the Mn and Sb hyperfine tensors the resonance spectra were measured in a DC field perpendicular to the film plane. As the magnetisation is rotated towards the c axis, the quadrupole splitting varies, in first order, as $3\cos^2\theta - 1$, where θ is the angle between the effective resonance field and this axis. Since the isotropic part of the hyperfine field due to the Fermi contact term is predominant, the Mn hyperfine field remains almost antiparallel, and the Sb hyperfine field parallel, to the magnetisation during the rotation. The angle θ was calculated from the equilibrium condition for magnetisation under an applied DC field H as (Le Dang *et al* 1986)

$$H = (4\pi M - H_{A1} - H_{A2})\cos\theta + H_{A2}\cos^3\theta \tag{1}$$

where the anisotropy fields H_{A1} and H_{A2} are defined by the relations

$$H_{A1} = (2K_1/M) \qquad H_{A2} = (4K_2/M).$$

For the cluster sample, 4π in equation (1) should be replaced by a factor N_{ef}.

The total quadrupole splitting is given by the expression

$$\Delta\nu(\theta) = \nu_Q(3\cos^2\theta - 1)/2 \tag{2}$$

with $\nu_Q = (3e^2qQ/20h)$ for spin $I = \frac{5}{2}$.

From the NMR data in zero external field, ν_Q is deduced to be 14 MHz and 44 MHz for ^{55}Mn and ^{121}Sb resonance lines, respectively.

For hexagonal crystals, H_{A2} can be several kilooersteds, e.g. 2 kOe and 4.7 kOe for MnSb and HCP Co, respectively. Thus the term $H_{A2}\cos^3\theta$ in equation (1), at the magic angle, is of the order of 1 kOe. The Mn and Sb linewidths decrease to a minimum at about H_0 = 7 kOe and 9 kOe for the samples with t_{Mn} = 2 Å and 12 Å, respectively (figures 3 and 4). It is clear that H_0 is mainly determined by the first term in equation (1). Taking $4\pi M$ as the bulk value and H_{A2} successively equal to 0, 1, 2, 3, 4 and 5 kOe, we selected the value which gives the best fit with experiment (table 1). As seen in equation (1), H_{A2} is expected to have an appreciable effect only when θ is small, i.e. for $H > H_0$. Indeed, the calculated curves nearly coincide in the low-field region ($H < H_0$) for H_{A2} = 1 and 3 kOe. Additional broadenings due to an inhomogeneous distribution of the hyperfine field and a spatial fluctuation of the magnetisation direction are expected for polycrystalline film samples. Using the H_{A1}- and H_{A2}-values in table 1, we calculated the shift in the resonance frequency due to the DC and demagnetising fields. Within the above approximation, only their projections onto the hyperfine field are taken into

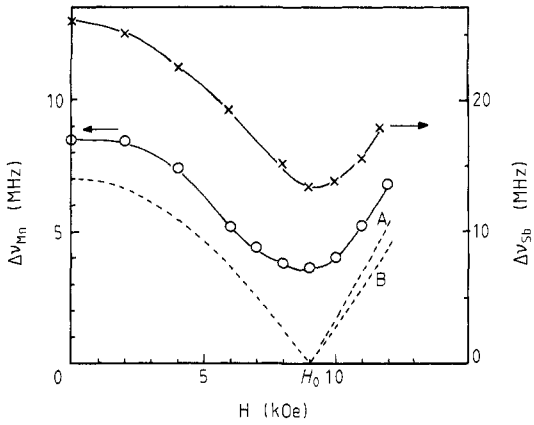

Figure 4. Variation in the Mn and Sb linewidths at half-maximum as functions of a DC magnetic field applied perpendicular to the film plane: — — —, theoretical variation in the total quadrupole splitting with $\nu_Q = 14$ MHz. A, B as figure 3, $t_{Mn} = 12$ Å.

Table 1. Anisotropy fields $H_{A1} = (2K_1/M)$ and $H_{A2} = (4K_2/M)$ deduced from NMR experiments at 4 K on MnSb film compared with the bulk values (Okita and Makino 1968).

Samples	H_{A1} (kOe)	H_{A2} (kOe)
Bulk at 77 K	−4.5 (52.8 at.% Mn)	≃2 (52.8 at.% Mn)
Bulk at 77 K	−10.5 (51.4 at.% Mn)	
(120, 12)[27]	−8 ± 2	3 ± 2

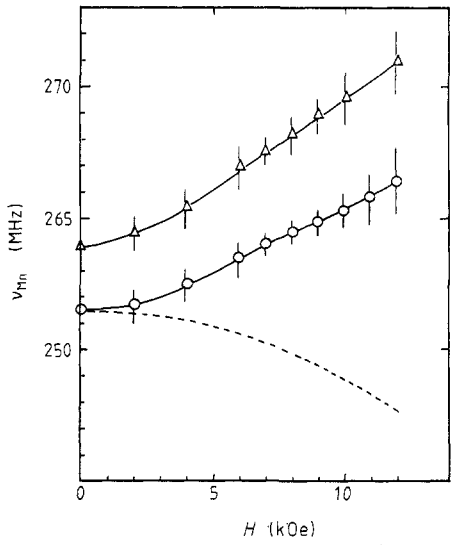

Figure 5. ^{55}Mn nuclear resonance frequency as a function of a DC magnetic field applied perpendicular to the film plane: — — —, theoretical frequency shift due to the DC and demagnetising fields. △, $t_{Mn} = 2$ Å; ○, $t_{Mn} = 12$ Å.

account. The anisotropic part of the effective field is then given by the difference between the calculated curve and the experimental points (figure 5). It should be recalled that the Mn and Sb effective fields are antiparallel and parallel, respectively, to the magnetisation. Finally the variation in the magnitude of the effective field H_{ef} as a function

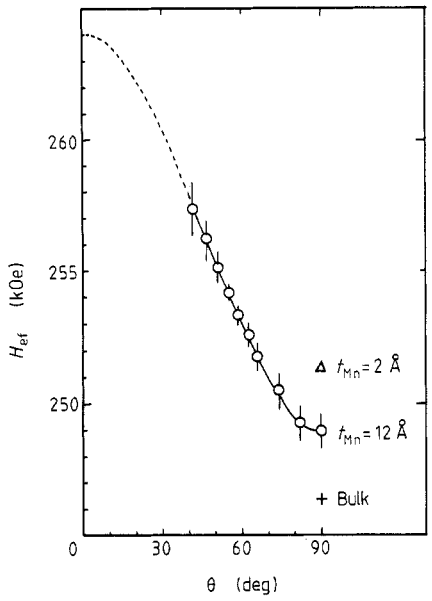

Figure 6. Magnitude of the Mn effective field H_{ef} as a function of the deviation angle θ from the c axis.

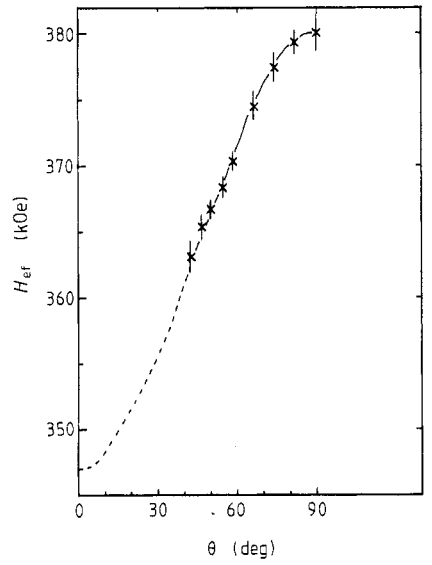

Figure 7. Magnitude of the Sb effective field H_{ef} as a function of the deviation angle θ from the c axis.

of the deviation angle θ from the c axis is obtained (figures 6 and 7) according to the theoretical expression

$$H_{ef} = (H_{\parallel}^2 \cos^2 \theta + H_{\perp}^2 \sin^2 \theta)^{1/2}. \tag{3}$$

For the sample with $t_{Mn} = 12$ Å the $H_{\perp}$ value is obtained from the resonance frequency in zero external field and the $H_{\parallel}$ value is estimated from the calculated curve. Thus the $H_{\perp}$ and $H_{\parallel}$ values were found to be: (i) 249 and 264 kOe for the Mn site, and (ii) 380 and 347 kOe for the Sb site. For the sample with $t_{Mn} = 2$ Å the shifts of the Mn and Sb lines (figures (1) and (2)) partially arise from a cluster demagnetising field.

4. Discussion

For a weakly anisotropic field, equation (3) can be written

$$H_{ef} = H_{iso} + [(H_{an} + H_d)/2](3\cos^2\theta - 1) \tag{4}$$

where H_{iso} and H_{an} are the isotropic and anisotropic parts, respectively, of the hyperfine field. H_d is the lattice dipolar field along the c axis. H_d was calculated to be +3.2 kOe and −1.3 kOe for Mn and Sb sites, respectively. It is obvious that the observed anisotropy in the effective field arises almost from H_{an}. For the Mn hyperfine interaction both the spin dipolar term and the anisotropy in the g-factor are expected to contribute to H_{an} (Freeman and Watson 1965). For Sb atoms the dipolar hyperfine interaction is due mainly to the unpaired spin on different p orbitals of the valence 5p electrons (Abragam and Pryce 1951). If we assume, to a first approximation, that the charge and spin asymmetries are the same, the spin dipolar field is simply equal to $q\mu_B$ where eq is the electric field gradient (Perlow *et al* 1965). In this way the dipolar fields estimated from the nuclear quadrupole couplings are equal to 17.7 kOe and 36 kOe in *absolute value* for Mn and Sb, respectively, with the ^{55}Mn and ^{121}Sb quadrupole moments Q taken as 0.35 b and 0.53 b, respectively. These spin dipolar fields roughly agree with the observed H_{an} values of −13 kOe and 21 kOe.

5. Conclusion

We have succeeded in measuring the Mn and the Sb hyperfine tensors and the effective anisotropy field in MnSb films by observing the field dependence of the quadrupolar broadening through the magic angle. It was shown that the anisotropic field H_{an} and the electric field gradient at the Mn sites probably originate mainly from 3d spin and charge asymmetries. The magnetocrystalline anisotropy of the annealed film is close to that of single-crystal samples.

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