Pramana - J. Phys., Vol. 36, No. 2, February 1991, pp. 221–229. © Printed in India.

Thermopower anisotropy in magnetic films of Co and Ni plated in presence of an external magnetic induction

BENU SINHA and AMAR NATH NIGAM
Department of Physics, Harcourt Butler Technological Institute, Kanpur 208002, India

MS received 11 January 1989; revised 15 October 1990

Abstract. Electroplated films of cobalt and nickel were grown on copper substrate both in absence and presence of external magnetic induction ranging from 25 to 72 gauss. The latter films showed a magnetic behaviour and an anisotropy in thermopower with respect to the direction of magnetisation.

Keywords. Anisotropy; thermopower; magnetic behaviour.

PACS Nos 75·70; 73·90; 72·20

1. Introduction

If a thin film of a ferromagnetic metal or alloy is grown in presence of an externally applied magnetic induction, the resulting polycrystalline film shows magnetic anisotropy. Girrard (1967) was the first to carry out this kind of work where he used a transverse field of 60 oersted while electroplating permalloy films. The magnetic properties of such films were found very useful in computer memories and have been reviewed by Cohen (1970) and Soohoo (1965). Druckzewski and Ausloos (1980) studied such magnetic films near the Curie point and detected the anisotropy in electrical resistivity quite apart from the magnetic anisotropy. Cu–Ni thin films show anisotropy near 300–402°K (Gyorgy *et al* 1980). Babkin *et al* (1984) grew single crystal magnetite films from vapour phase on the surface of a magnesium oxide single crystal, both in presence and absence of external magnetic induction. These films showed different properties. Kornev *et al* (1985) annealed Co-films in presence of 100 Oe magnetic induction and studied the angular variation of RF field absorption which was correlated to the anisotropy of electrical resistance.

The entire literature cited above refers either to evaporated or sputtered films either grown or annealed in presence of a magnetic induction. The present paper deals with the electroplated films of Co and Ni deposited on the copper substrate foils in presence of an externally applied magnetic induction. Such films show an anisotropy in the thermopower.

Our interest in the electroplated films grew because they exhibit a phenomena similar to the classical size effect even in the micron range of thickness (Prakash and Nigam 1989). The magnetic films of Ni however show an EXAFS structure different from that of films grown without magnetic field (Sinha and Nigam (1990a) under publication).

2. Experimental

(a) *Substrate preparation*

Copper foils (50 μ thick) were cut into 5 cm × 5 cm square pieces and cleaned by heating in hot benzene vapour and then boiling in KOH solution and distilled water. Thereafter they were electropolished as anodes in an orthophosphoric acid bath with a stainless steel cathode using a current of 300 mA for a few minutes. The electropolished foils were washed in distilled water and then in methanol.

(b) *Electroplating*

Plating methods have been described earlier by us (Sinha and Nigam 1990b) both in the absence and in presence of external magnetic induction. In the absence of magnetic induction, plating current was 10 mA. As soon as magnetic induction was applied the current fell considerably and was raised up to 100 mA in Ni deposition and up to 1·5 A in case of Co-deposition. Even then the plating times were considerably enhanced. This kinetics has also been described earlier (Sinha and Nigam 1990b). The plating thickness was controlled by time of plating and was determined by weighing.

(c) *The thermopower measurements*

The foils plated in absence of magnetic induction (**B**) were cut into 2 mm wide strips for thermopower measurements. Thermopower was measured using a circuit shown in figure 1. An ice-cooled brass rod with a small cup machined at its top end holding

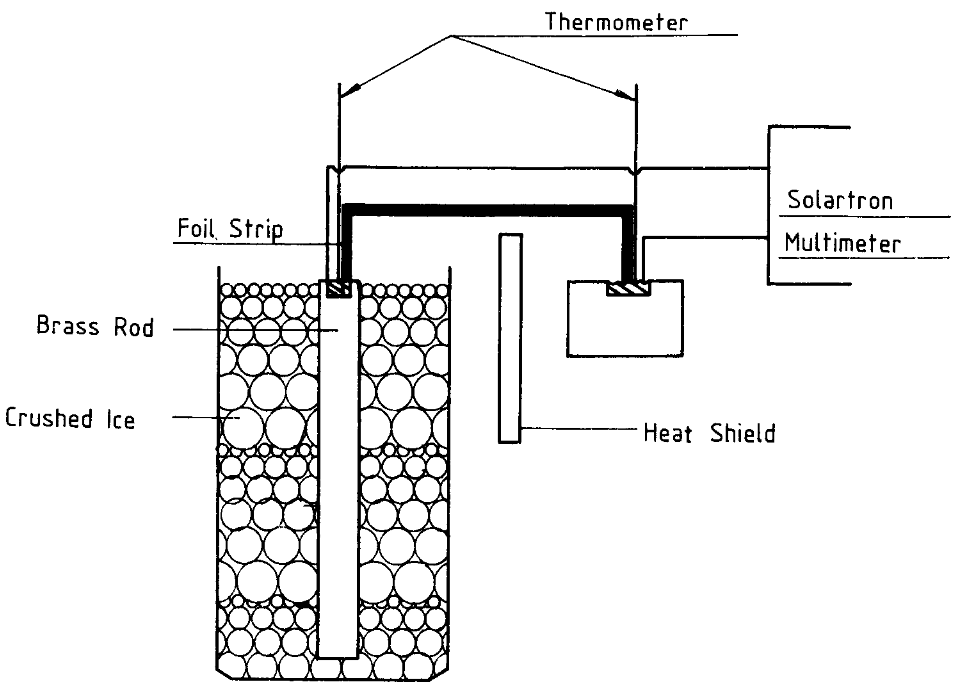

Figure 1. Circuit for measuring thermopower.

some mercury, was used as a cold junction. The plated strip and a copper wire dipped in the cooled mercury formed this cold junction. The other end of the plated strip was dipped in a mercury cup maintained at room temperature and formed the hot junction. The thermopower leads were fed to a digital microvoltmeter, Solartron model 7150 capable of reading up to 0·1 μV. The temperature at both the junctions were recorded by thermometers dipped in the mercury cups. Temperature recording was done throughout the experiments. Whatever be the direction of cut of the strip the measured value of the thermopower was the same as long as the thickness of the plating was constant.

In the case of foils plated in presence of the external magnetic induction, strips were cut (a) along the magnetisation direction, (b) at direction making different angles with the magnetisation direction and (c) at right angles to the magnetisation direction. These strips which showed a constant thickness throughout revealed an anisotropy in the thermopower i.e. variation with the angle of cut. Since this magnetisation persists even after removal of the original **B** field used during electroplating one attributes this anisotropy to the magnetisation of the film induced during growth.

3. Evaluation of the film thermopower

Canon* has derived a formula to evaluate the thermopower of a system consisting of a cylinder of one conductor surrounded by an outer plated layer of another conductor. A copper wire electroplated with nickel is an example of this kind. The thermopower of such a system has been derived as

$$Q_{\text{system}} = Q_{\text{subs/Cu}} + \frac{Q_{\text{film/Cu}} - Q_{\text{subs/Cu}}}{1 + \dfrac{\rho_{\text{film}}}{\rho_{\text{subs}}} \cdot \dfrac{S_{\text{subs}}}{S_{\text{film}}}}, \tag{1}$$

here 'subs' stands for substrate, ρ for resistivity, S for area of cross-section. This equation was verified earlier for Cu wires plated with nickel (Misra and Nigam 1982).

To adapt this equation for strips we first made calculation for a Cu-strip plated only on one side. If the strip width is b and its thickness is a and the Ni-film thickness is t, (1) takes the form:

$$Q_{\text{system}} = Q_{\text{subs/Cu}} + \frac{Q_{\text{film/Cu}} - Q_{\text{subs/Cu}}}{1 + \dfrac{\rho_{\text{film}}}{\rho_{\text{subs}}} \cdot \dfrac{a}{2t}}, \tag{2}$$

where b cancels out being the common width of Cu and Ni. ($S_{\text{subs}} = ab$, $S_{\text{film}} = b.t$). The corresponding calculation for a Cu-strip plated on both the sides gave

$$Q_{\text{system}} = S_{\text{subs/Cu}} + \frac{Q_{\text{film/Cu}} - Q_{\text{subs/Cu}}}{1 + \dfrac{\rho_{\text{film}}}{\rho_{\text{subs}}} \cdot \dfrac{ab}{(a+b)t + 4t^2}} \tag{3}$$

t^2 can be neglected because $b = 2\,\text{mm}$ and $a = 50\,\mu\text{m}$. Further since $a + b \sim b$, (3) reduces to (2) in the first approximation.

*Canon A, private correspondence. The full derivation is being avoided for brevity.

Our substrate and the leads are of copper, (2) reduces to

$$Q_{\text{system}} = \frac{Q_{\text{Ni-film/Cu}}}{1 + \dfrac{\rho_{\text{Ni-film}}}{\rho_{\text{Cu}}} \cdot \dfrac{a}{2t}} \tag{4}$$

here $a/2t$ is the ratio of Cu-foil thickness to the total Ni-film thickness (t on each side).

Knowing the measured Q_{system} one can evalute $Q_{\text{Ni-film/Cu}}$. Now, Q_{system} is about 10 times $Q_{\text{Ni-film/Cu}}$ and was measured correct up to 0·03 μV/°C. Thus $Q_{\text{Ni-film/Cu}}$ is correct up to 0·3 μV/°C. Our variations exceed this value.

4. Results and discussion

Our observations involve three parameters with respect to which the measured thermopower varies with (a) the different angles with respect to the magnetisation direction along which the strips were cut (figures 2 and 3); (b) the magnetic induction B applied during electroplating because this will decide the magnitude of magnetisation (figures 4a, b); (c) the thickness of the deposit (figure 5).

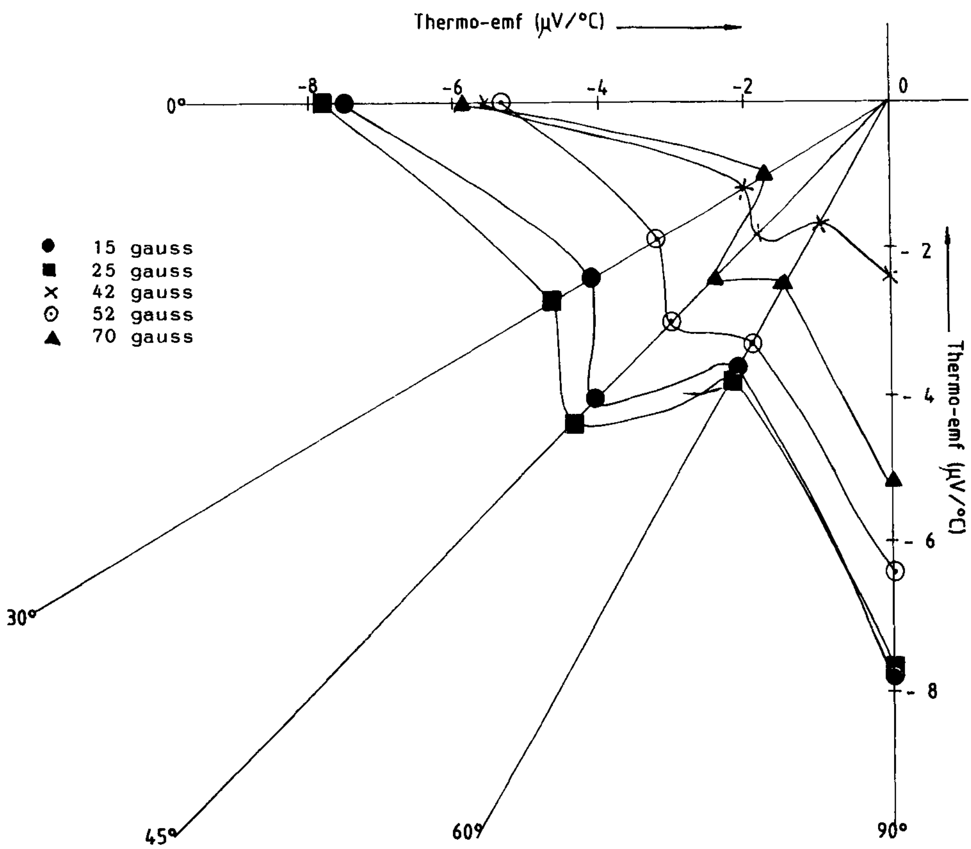

Figure 2. Angular variation in thermopower of magnetic film of Ni, 10 μm thickness (maximum thickness attained).

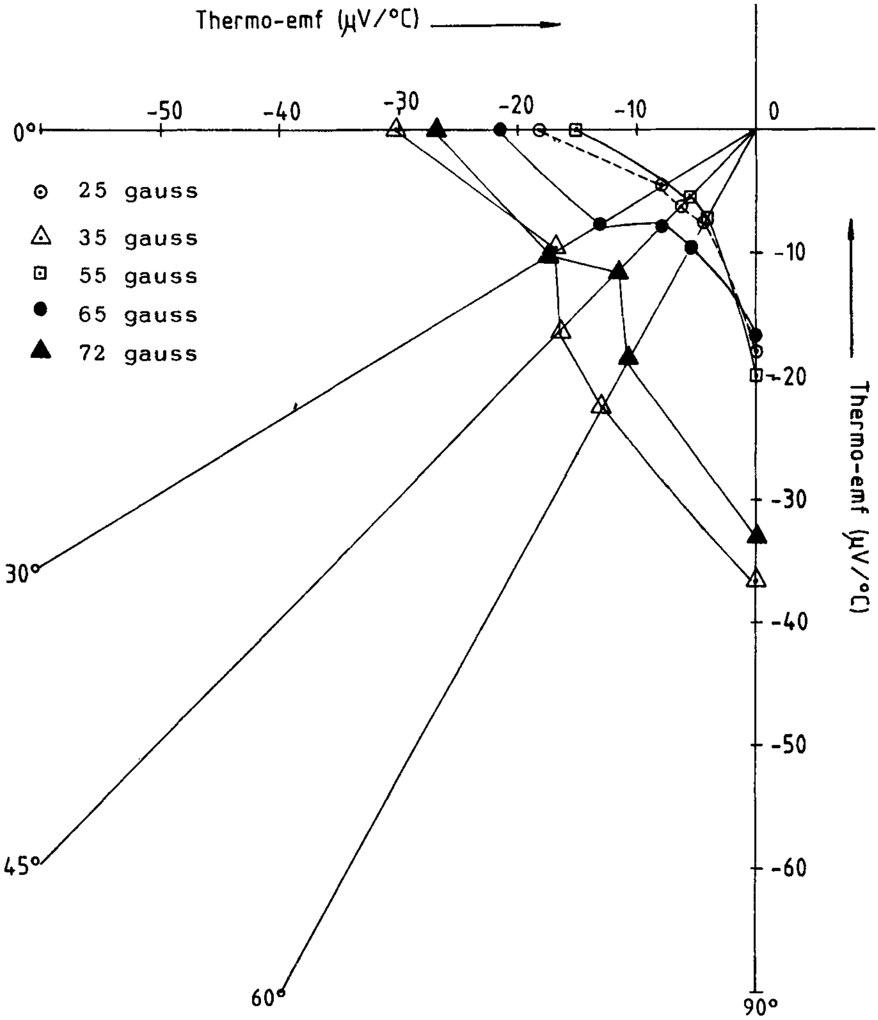

Figure 3. Angular variation in thermopower of magnetic film of Co, 4 μm thickness (maximum thickness attained).

(a) *The angular dependence*

The polar plots* in figures 2 and 3 describe the angular variation in thermopower with respect to the direction of magnetisation for Ni and Co respectively. Each figure corresponds to a fixed film thickness used and different curves in each figure to different **B** values used during electroplating. The distance from the origin represents the thermopower evaluated by (4) and θ is the angle of direction of cut of the strip. Our results on thermoelectric anisotropy are very much similar to those of Kornev *et al* (1985) on electrical resistivity.

Various causes of magnetic anisotropy have been reviewed by Cohen (1970). In polycrystalline films the two main causes are strain magneto anisotropy and pair ordering anisotropy. Since the films plated in the absence of **B** field do not show any

*Only one figure each is given for brevity.

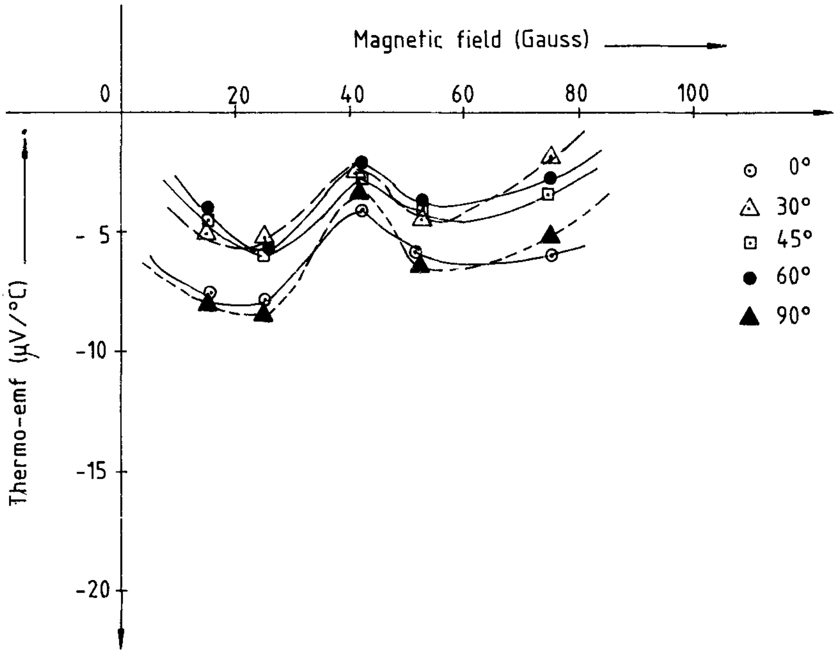

Figure 4(a). Variation in thermopower with **B** for various directions in a film of constant thickness (10 μm Ni film).

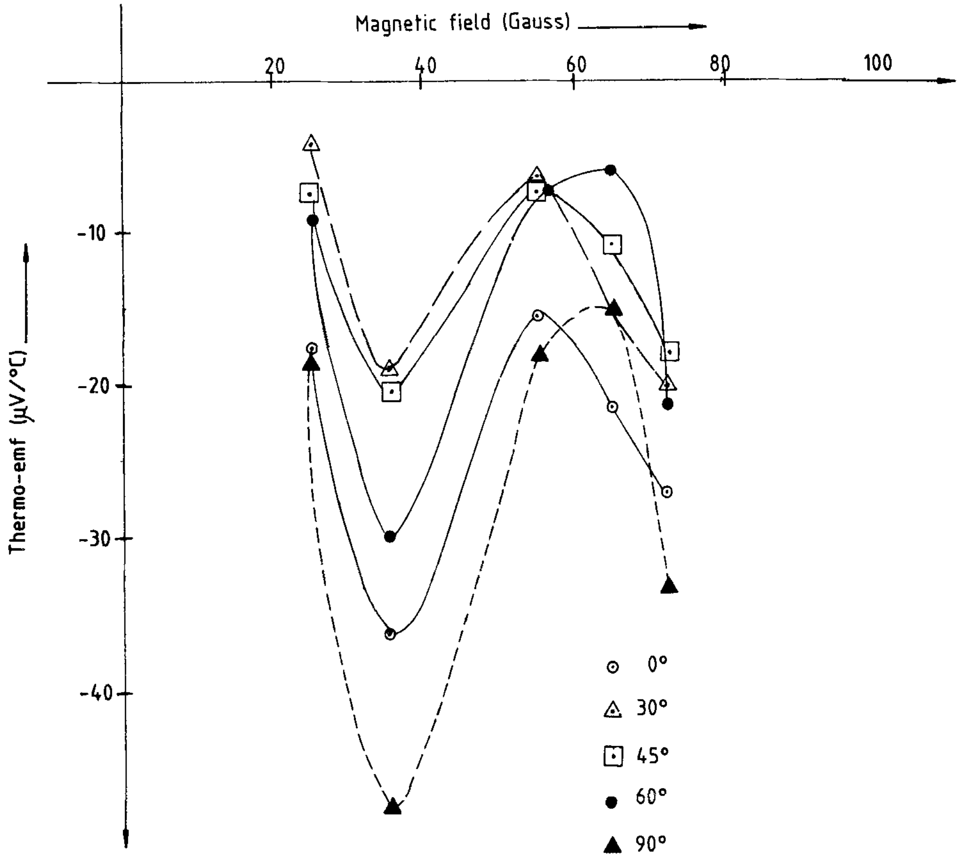

Figure 4(b). Variation in thermopower with **B** (4 μm Co film).

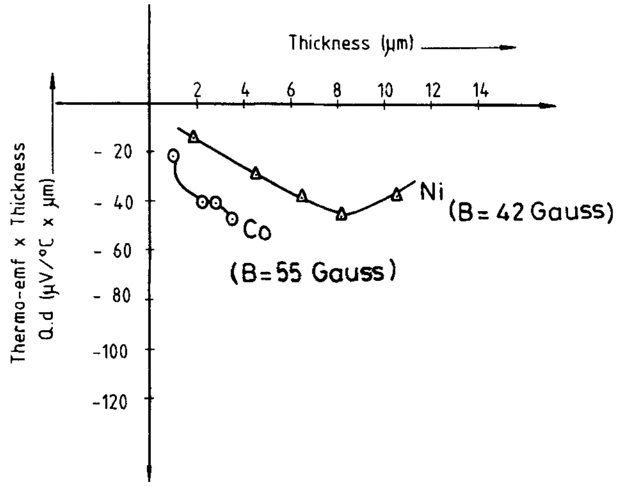

Figure 5. Thickness effect in electroplated films of Ni and Co.

anisotropy (but are still under a strain (Misra and Nigam 1987)) the first cause is less probable than the second. The pair ordering anisotropy was suggested to explain the anisotropic behaviour of the ferromagnetic films annealed in a magnetic field and then suddenly quenched to room temperature. A uniaxial magnetic anisotropy results. The function of the applied magnetic induction **B** is to align **M** the magnetisation direction everywhere in the sample. This alignment persists even if the induction is removed.

Another important factor mentioned by Cohen (1970) is the aging effect due to impurities. This gives rise to a time-dependence of anisotropy with a relaxation time of a few days. We measured our anisotropy after a gap of a few months and found no change. Thus the aging effect is not present in our samples.

Oblique incidence anisotropy is also ruled out because in our case the direction of plating current was always perpendicular to the copper foil surface.

Observations similar to ours were reported by Kornev *et al* (1985) on the resistivity of cobalt films annealed in a magnetic field of 100 oersted. They related this anisotropy to (a) dispersion in the direction of magnetisation (b) anisotropic shape of cobalt crystallites. The dispersion in magnetisation direction is caused by the structural defects formed during growth. In our case the electroplated metals are nickel (*fcc*) and cobalt (*hcp*) on copper (*fcc*). Usually the nickel crystallites being *fcc* will not have anisotropy due to geometrical shape, only spin anisotropy will be present. However, the nickel film crystallites deposited on copper will deviate from *fcc* structure due to strains caused by a mismatch between copper and nickel lattice parameters. Our observations can also be interpreted on the lines suggested by Kornev *et al* (1985).

(b) *Thickness dependence*

A direct plot of thermopower variation with thickness always results in complicated curves. A better method is to verify Mayer's relation (Mayer 1959) for the classical size effect

$$Q(t) = \alpha + \beta/t, \tag{5}$$

where t is film thickness as before and α, β are constants. Thus a plot of t. $Q(t)$ vs t

results in a straight line. Figure 5 shows such plots for Ni and Co films. The slope of the straight line is dependent on the angle of cut of the strip and also field **B**. In our case quite a few films gave a non-linear fit.

Thus the classical size effect analogue in electroplated films exists even in the micron range of film thickness in contrast to evaporated films where the size effect is absent beyond 1000 Å thickness.

5. Conclusions and further scope

Co and Ni films electrodeposited in presence of an external magnetic induction are known to be magnetically anisotropic and also found to be electrically anisotropic. They show an anisotropy in thermopower. The films being polycrystalline, their anisotropy is attributed to the dispersion in magnetisation direction caused by defects in the lattice grown during electrodeposition. Co and Ni films grown at the same B value show different kinds of anisotropies.

However, there are certain aspects which are not accountable at present. In figure 2, the angular variation in thermopower for $10\,\mu$m Ni film is shown. Figure 3 shows the above variation for a Co-film $4\,\mu$m thick. In the case of Ni the thermopower is maximum at 45° direction of cut with respect to the **B** direction while, it is minimum in Co at this angle except at 35 gauss field where the minimum lies at 30°.

At first sight figures 2 and 3 appear similar but they do not show exactly the same kind of angular variation for different **B**-values used and one can easily suspect them to be random. In figure 4(a, b) are shown variations in thermopower with applied **B** fields for a film with constant thickness but along a different direction. The general nature of these curves is quite similar and shows an alternating effect which is dependent on the direction as well. Thus in figures 2 and 3 two kinds of variations have been included—one with direction and the other with field. The nature of both is different and hence this resolution is necessary.

An exact theory cannot be developed until the structure of these films is examined by electron diffraction in reflection setting or by neutron diffraction.

As a matter of fact no theory for the effect of a magnetic field on the thermopower of ferromagnetic metals is found in the literature but for an old paper by Sondheimer (1948) based on an over simplified two band model. Sondheimer however cautions against applying his formulae to the ferromagnetic metals.

References

Babkin E V, Dorkin N A, Koval K P and Pynko V G 1984 *Sov. Phys. Solid State (Engl. Transl)* **26** 1404

Cohen M S 1970 *On Ferromagnetic properties of thin films* (eds) L I Maissel and R Glang 'Handbook of thin film Technology, (New York: McGraw Hill) Ch. 17

Druckzweski K and Ausloos M 1980 *J. Magn. Magn. Mater.* **15–18** 927

Girrard R 1967 *J. Appl. Phys.* **38** 1423

Gyorgy E M, Dhillon Jr J F, Mcwhan D B, Rupp Jr L W and Testradi L P 1980 *Phys. Rev. Lett.* **45** 57

Kornev Yu V, Sementsov D I and Sidorenkov V V 1985 *Sov. Phys. Dokl. (Engl. Transl)* 1986 **30** 801

Mayer H 1959 in *Structure and Properties of thin films* (ed.) Naugebauer, (New York and Vermilyea: John Wiley and Sons Inc.) p. 225

Misra K K and Nigam A N 1982 *Phys. Status Solidi* **73** 559

Misra K K and Nigam A N 1987 *Nat. Sci. Acad. Lett.* **10** 27
Prakash (Miss) Benu and Nigam A N 1989 *Indian J. Phys.* **A 63** 574, 648
Sinha (Mrs) Benu and Nigam A N 1990a *X-Ray Spectrometry* (under Publication)
Sinha (Mrs) Benu and Nigam A N 1990b *J. Electrochem. Soc. India* **39** 26
Sondheimer E H 1948 *Proc. R. Soc. (London)* **A193** 484
Soohoo R F 1965 *Magnetic thin films* (New York: Harper and Row Publishers Inc.)