

## Thermoelectric and Hall effect studies in a hydrogenated foil of nickel

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Variations in Hall voltage in a hydrogenated thin foil of nickel as the system loses hydrogen with time have been recorded. It is seen that the sign of the charge carried in a hydrogenated sample remains negative. This fact cannot account for the sign reversal in thermoeffect of these foils. It is suggested that the change in sign of  $dn/dE$  curve due to surface states of chemisorbed hydrogen might be responsible for the thermoeffect sign reversal.

### 1. INTRODUCTION

In an earlier note (Nigam & Ram 1975) we reported the effect of hydrogen diffusion on the thermoelectric behaviour of thin nickel foils subjected to electrolytic hydrogen diffusion. Such foils loose hydrogen with time when left to themselves. During this out-gassing period the variation in thermoeffect was recorded. It was found that the fully hydrogenated sample of nickel foil showed a reversal in sign of the thermoeffect. For ready reference these results are reproduced in Fig. 1. In order to account for this sign reversal we made use of the thermoeffect formula for a two band system (Nigam & Garg 1972)

$$\frac{d\theta}{dT} = -\frac{\sigma}{\epsilon} \quad \dots \quad (1a)$$

where

$$\sigma = \frac{\pi^2 k^2 T}{\zeta} \left[ \frac{1}{3} \frac{\pi^2 k^2 T}{\zeta^2} \left( \frac{\partial n_s}{\partial E} + \frac{\partial n_a}{\partial E} \right) \right] \quad \dots \quad (1b)$$

$T$  is the absolute temperature,  $k$  the Boltzmann constant,  $\zeta$  the Fermi energy,  $n$  the density of states of the electron in the band whose suffix is added to  $n$  and  $E$ , the energy of the band. The sign reversal could be due to (a) either the change in sign of  $dn/dE$ , (b) or due to change in sign of  $\epsilon$ , the charge of carrier of electricity. Thus a Hall Effect measurement can decide whether or not the proposition (b) is true. The present note reports these measurements.

### 2. EXPERIMENTAL

Hall Effect measurements were carried out on  $4\mu$  foils cut to  $5 \text{ cm} \times 0.5 \text{ cm}$  size and subjected to hydrogen diffusion by electrolysis as described earlier

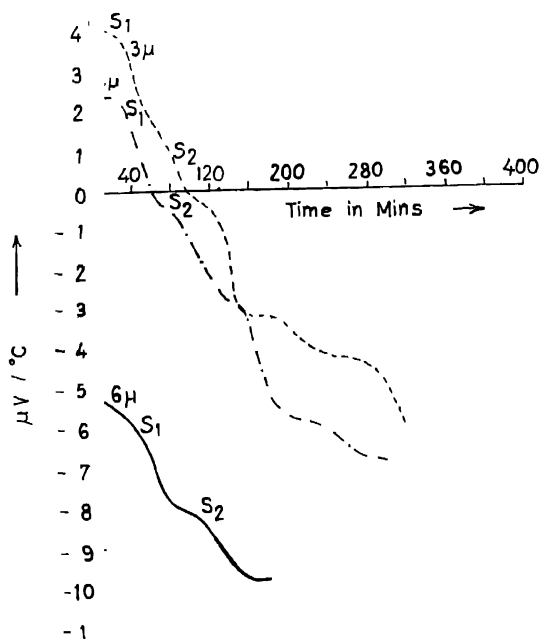


Fig. 1. Thermo emf variation with time for the foil after hydrogenation (curves for different thicknesses are shown)

Nigam & Rani (1975) The Hall voltage leads were wires also made of nickel. The measuring device for the Hall voltage was a potentiometer with a least count  $10^{-6}$  volts. The pole pieces were 13 cm in diameter with a gap 1.9 cm. A magnetic field 12.3 Kilogauss (max value) could be applied along the foil thickness. The current leads were copper wires joined mechanically to the sample. A current of 150 mA was passed along the length of the sample from two batteries each of 6 volts connected in parallel.

Our object was to follow the changes in the Hall voltage with time as the sample loses hydrogen. We carried out the following operations each time :

- Zero field ( $B = 0$ ) transverse voltage was recorded.
- A field 12.3 Kilogauss was applied and again the transverse voltage measured.
- Field was reversed and the observations (a, b) repeated

d) Current was reversed and all the above steps *a, b, c* repeated. It took 5 minutes to take the above set of eight observations, which were repeated each time after the intervals indicated in Fig. 2. Ideally one ought to stabilize a ferro-magnetic system for an hour each time an observation is taken. However for a sample losing hydrogen with time this is too long a period. Further, a freshly hydrogenated sample is not ferro-magnetic but diamagnetic (Baner & Schmidbauer 1961). The field stabilisation is therefore not necessary in the beginning.

### 3. DISCUSSION

As seen in Fig. 2 the Hall voltage remains negative on hydrogen diffusion. We therefore conclude that the sign of the charge carriers does not change by the

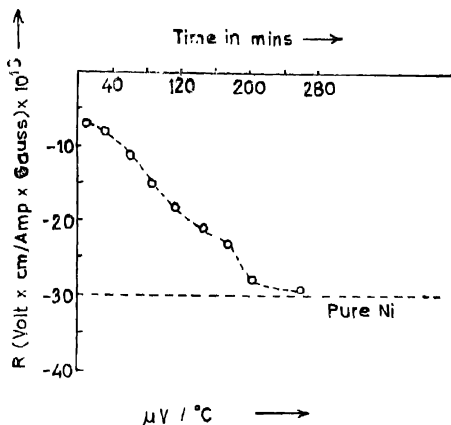


Fig. 2. Observed variation in Hall constant  $R$  with time for nickel foil after hydrogenation

presence of hydrogen. We are therefore left with the first proposition. Change in sign of the gradient  $dn/dE$  must be responsible for the reversal in the sign of the thermomf. How to account for this in nickel foils where the  $d$ -band remains partially filled even after hydrogen diffusion? We take shelter of a new idea. In our recent studies on the electrical conduction in hydrogenated nickel foils Nigam & Ram (1977) we have established that the  $dn/dE$  curve for the  $d$ -band is not adequate enough to account for the observed variations in resistivity with the time of hydrogen diffusion and that it is essential to bring into discussion the surface states formed by the chemisorbed hydrogen. If we do this, then there is a way out for our difficulty. The surface states begin after the Fermi

level (Horiuti & Toya 1969) Fig. 3 shows a tentative diagram where the dashed curve represents the proposed surface states. Clearly, if these states dominate the electrical properties of hydrogenated foil (where the surface to volume ratio is large) the  $(dn/dE)$  has an opposite sign with respect to the  $(dn/dE)_{d-band}$ . This indeed seems to account for the sign reversal

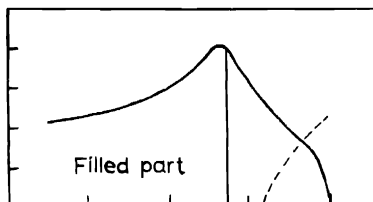


Fig. 3. Density of states curve for d-band, The dotted lines shows the tentative curve for surface density of states.

We may mention here one more fact. The Ni-foils used were supplied by M/s Goodfellow Metals, Cambridge, England. We have later on also used the foils supplied by M/s Vacuum Geschmelze, Hanau, West Germany. Foils of the same thickness show qualitatively the same variation of thermo emf with time of hydrogen outgassing but the curves corresponding to the latter foils are a little shifted downwards. We are not aware of the different methods of preparation of the foils employed by the two firms. However, to look for the surface effects we took a surface electron diffraction pattern. The two foils have different kind of surfaces. The former foils have a preferred orientation of crystallites at the surface while the latter show a random orientation. The surface states formation does depend on the orientation and for this reason the two sets of foils will show difference in magnitude of the sign reversal of thermo emf. This is only a qualitative discussion. The existing experimental data are rather too little to give a quantitative theory of this phenomena.

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