TRANSPORT PROPERTIES OF n-TYPE FERROMAGNETIC SEMICONDUCTOR $HgCr_2Se_4$ (*)

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ABSTRACT — Temperature dependence of the electrical resistivity (ρ), its temperature derivative and Seebeck effect were used to study the ferromagnetic transition in a $HgCr_2Se_4$ sample with n-type impurity. The Hall voltage has been separated in the so-called normal and extraordinary Hall contributions.

1 — INTRODUCTION

The chalcogenide spinel $HgCr_2Se_4$ is a ferromagnetic semiconductor in which the Cr^{3+} ions occupy the octahedral sites and the Hg^{2+} ions occupy the tetrahedral sites [1-4]. It undergoes a ferro-paramagnetic transition at about 110 K [1, 3]. The magnetic properties arise from the interaction of localised Cr^{3+} electrons with free electrons [1]. A competition between the opposing ferromagnetic super-exchange Cr-Se-Cr and antiferromagnetic super-exchange Cr-Se-Hg-Se-Cr also plays an important role in the magnetic properties of $HgCr_2Se_4$ [5]. One of the most striking features of ferromagnetic chalcogenide spinels is that their absorption edge shows anomalously large shifts as the

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temperature falls very low [6-8]; for example $HgCr_2Se_4$ absorption edge is 0.80 eV at room temperature and shifts to 0.27 eV at liquid helium temperature [7]. The temperature dependence of the absorption edge is non-linear, being remarkably high around the critical temperature (T_c) and nearly constant in the temperature range 180-300 K [7]. $HgCr_2Se_4$ exhibits anomalous electrical properties strongly dependent on the heat treatment of the sample [1]. $HgCr_2Se_4$ can be obtained by vapour transport reaction using Al + Cl as transport agent. $HgCr_2Se_4$ annealed in Hg is a n-type semiconductor in the whole temperature range studied [1]. In the following we present an experimental study of transport properties (electrical resistivity, Hall effect and Seebeck effect) as a function of the temperature in a n-type $HgCr_2Se_4$ sample with a very high concentration of free electrons. This study aims at correlating the electronic properties of $HgCr_2Se_4$ with the anomalous temperature dependence of its gap width in order to obtain a better insight into the magnetic properties of that system.

2 – EXPERIMENTAL

The n-type $HgCr_2Se_4$ sample we have studied was annealed in Hg. Its dimensions are $2.5 \times 2 \times 1.2$ mm and its resistivity is 202 mΩcm at 273 K.

Very accurate measurements of electrical resistivity were obtained with a 4 wire potentiometer method using a d. c. current with stability better than $5/10^6$ [9]. The voltage resolution in the detector was $\pm 10^{-2}$ μV. The Hall effect was measured with a lock' in a. c. technique [10]. The Seebeck coefficient was measured by the hot-point method using a copper-constantan thermocouple with a measuring junction of 0.1 mm in diameter [11]. The voltage resolution in the detectors is $\pm 10^{-2}$ μV.

3 – DATA ANALYSIS

As shown in figure 1(a) the electrical resistivity (ρ)of the n-type $HgCr_2Se_4$ crystal has an unusual temperature dependence, increasing as the temperature rises. The temperature derivative ($d\rho / dT$) of the resistivity is obtained by a sliding average rule [12]. This derivative reaches a maximum value at about 124 K

and as usual we take this temperature as the critical temperature (T_c) – figure 1(b). A minimum in $d\rho / dT$ occurs at around 180 K,

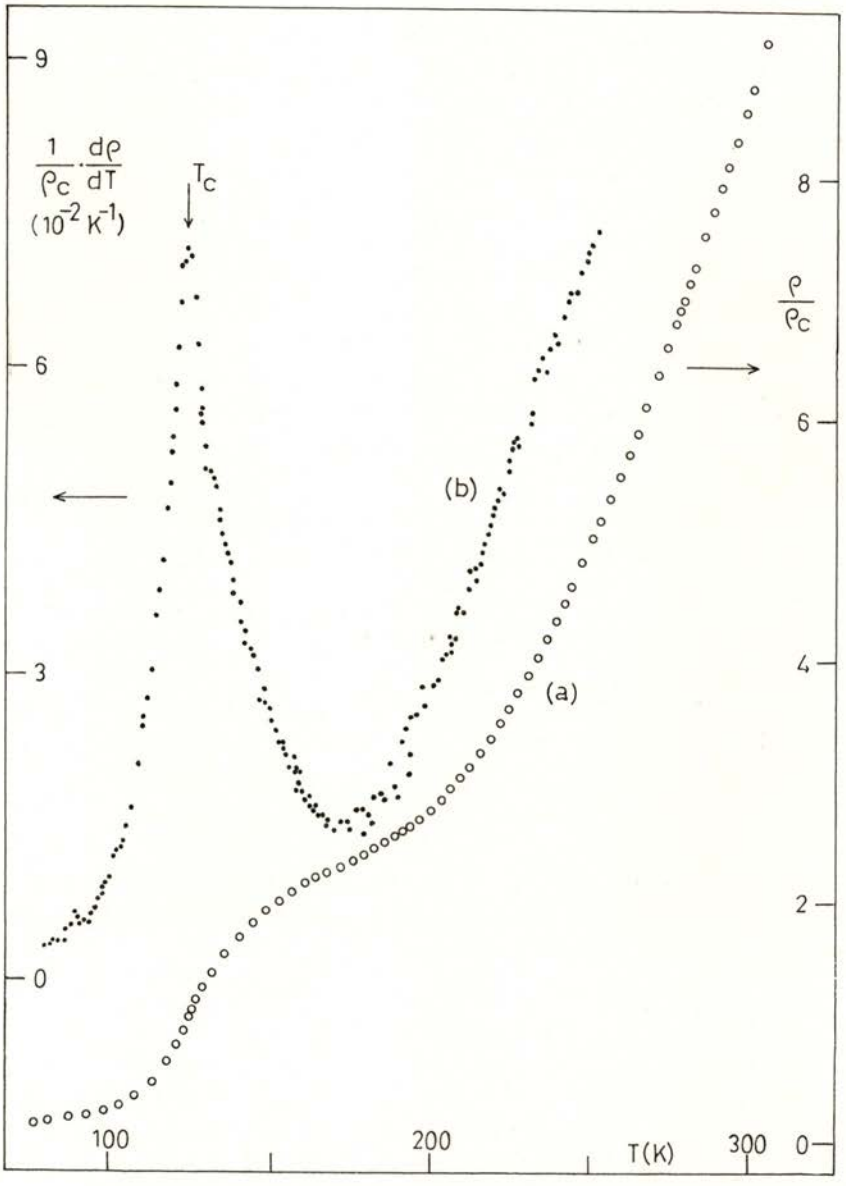

Fig. 1 — Temperature dependence of reduced resistivity (a) and thermal derivative of resistivity (b) of $HgCr_2Se_4$.

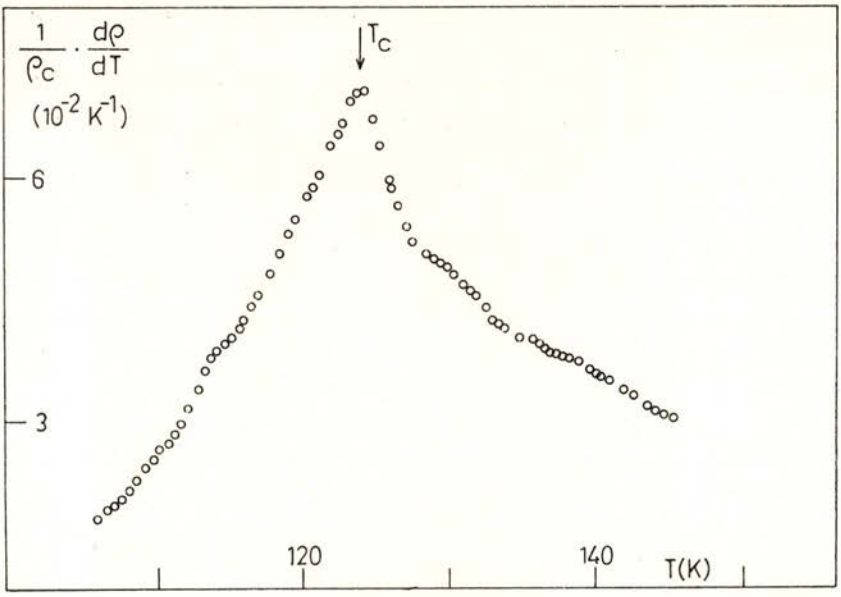

Fig. 2 — Temperature dependence of thermal derivative of resistivity near the critical temperature, $T_c = 124$ K, in an enlarged scale.

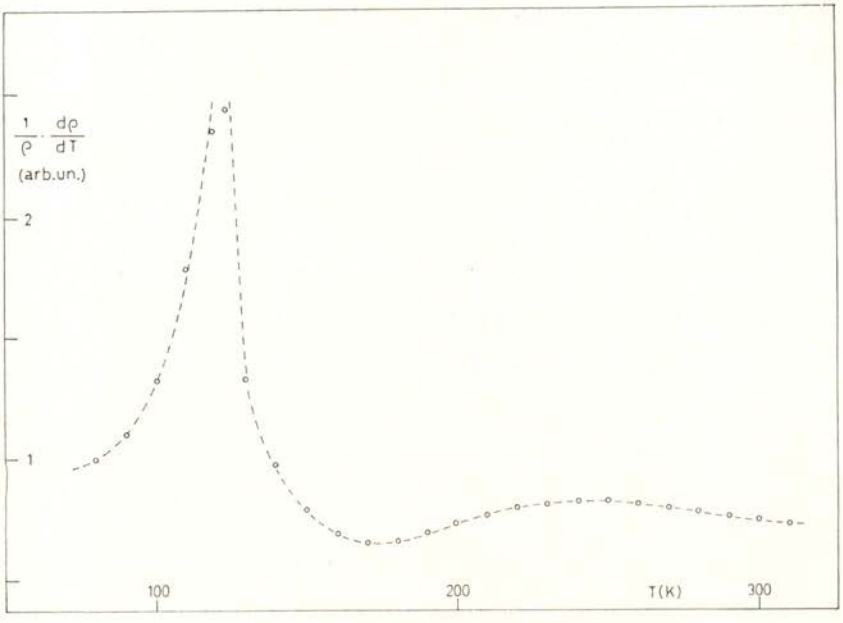

Fig. 3 — Temperature dependence of thermal derivative of log of resistivity ( ) of $HgCr_2Se_4$.

followed by a pronounced increase in $d\rho / dT$. The temperature derivative of ρ displays a striking asymmetric behaviour around T_c (figure 2). These results are quite similar to those previously reported although this asymmetric behaviour was not explicitly referred [13].

According to a model of spin-polarized bands, the exchange interaction between localized and band electrons results in a spin splitting of the conduction and valence bands [14]. In a first approximation the corresponding energy changes for each band are given by:

$$\Delta E_b^{\pm 1} = \mp \frac{1}{2} S J_b \frac{M(T)}{M(0)}$$

where S is the localized spin, J_b the exchange parameter for the b-labelled band, $M(T)$ the magnetization at the temperature T and ± 1 refers to the spin up or down. Let us suppose that changes in free carrier mobility are relatively small and so the anomalous variation in the electrical resistivity at the critical region is mainly due to concentration variation. Using this assumption and assuming the existence of a donor level of activation energy $E_d(T)$ we have

$$\rho(T) = \rho_0 \exp(-E_d / k_B T)$$

It seems plausible to assume that the activation energy of impurity levels varies with the temperature, accompanying the variation of the gap width. For simplicity sake let us suppose that $E_d(T) = E_0 - E_1 M(T)$, E_0 and E_1 constants. The temperature derivative of $\log \rho$ becomes

$$\frac{1}{\rho} \frac{d\rho}{dT} = \frac{1}{k_B T^2} (E_0 - E_1 M) + \frac{E_1}{k_B T} \frac{dM}{dT}$$

Near the critical temperature $M(T) \simeq 0$ and then we have approximately

$$(1/\rho)\, d\rho/dT \propto dM/dT$$

An anomalous behaviour of $(d\rho/dT) \cdot (1/\rho)$ similar to $|dM/dT|$ is predictable in the critical region and so the asymmetric behaviour in $d\rho/dT$ must be closely related to the asymmetric behaviour in dM/dT. In figure 3 we have a plot of $(d\rho(T)/dT)\,(1/\rho(T))$ versus T.

As the gap width (E_g) variation follows the magnetization variation, related to $E_d(T)$, it is natural to expect that ρ (T) is associated with E_g. In fact log ρ has a roughly linear dependence on E_g from 90 to 200 K, as can be seen in figure 4.

A fitting of the experimental values in the ferromagnetic region to the expression $(d\rho / dT) = A - B \log |\varepsilon|$ where A

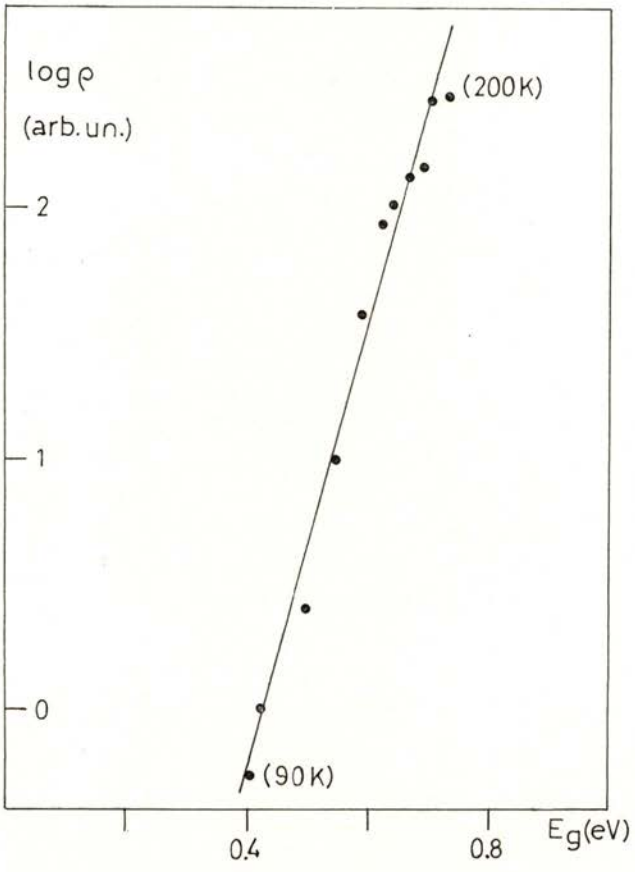

Fig. 4 — A plot of log ρ versus the gap width (E_g).

and B are constants and $\varepsilon = (T - T_c) / T_c$, defines $T_c = 123.7$ K, but it was not possible to fit the experimental data in the paramagnetic region near T_c, to such an expression. The log ρ as a function of the reciprocal of the temperature (figure 5) exhibits a complicated behaviour. In the high temperature region ($T \gtrsim 200$ K),

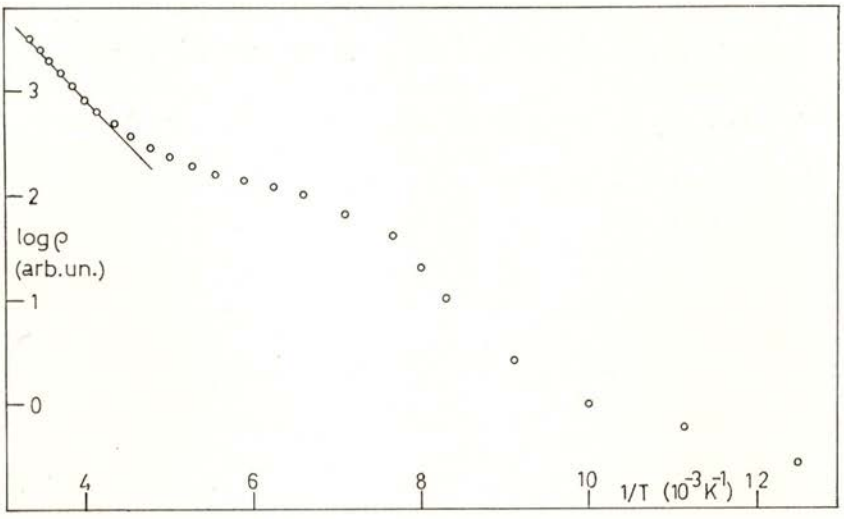

Fig. 5 — A plot of log ρ versus the reciprocal of the temperature.

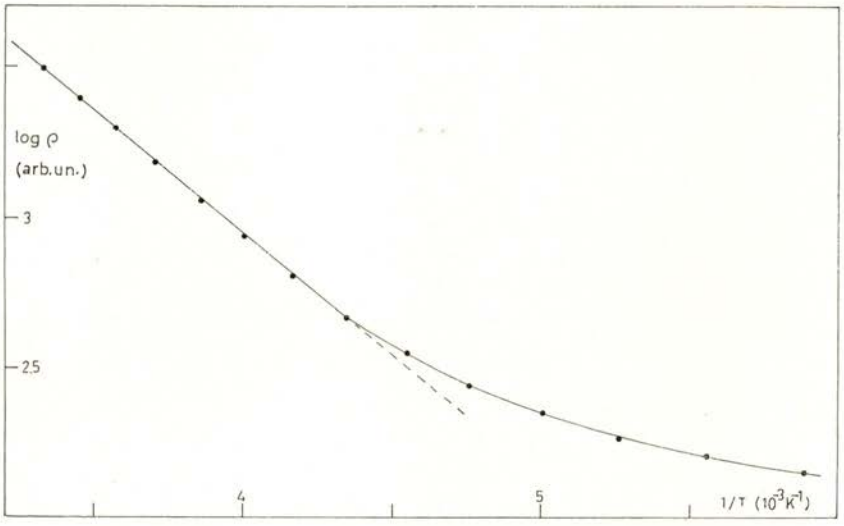

Fig. 6 — A plot of log ρ versus the reciprocal of the temperature in the range 170-300 K.

from the slope of the straight line we deduce a value of 0.071 eV for the activation energy of impurity levels in the 200-300 K temperature range (figure 6).

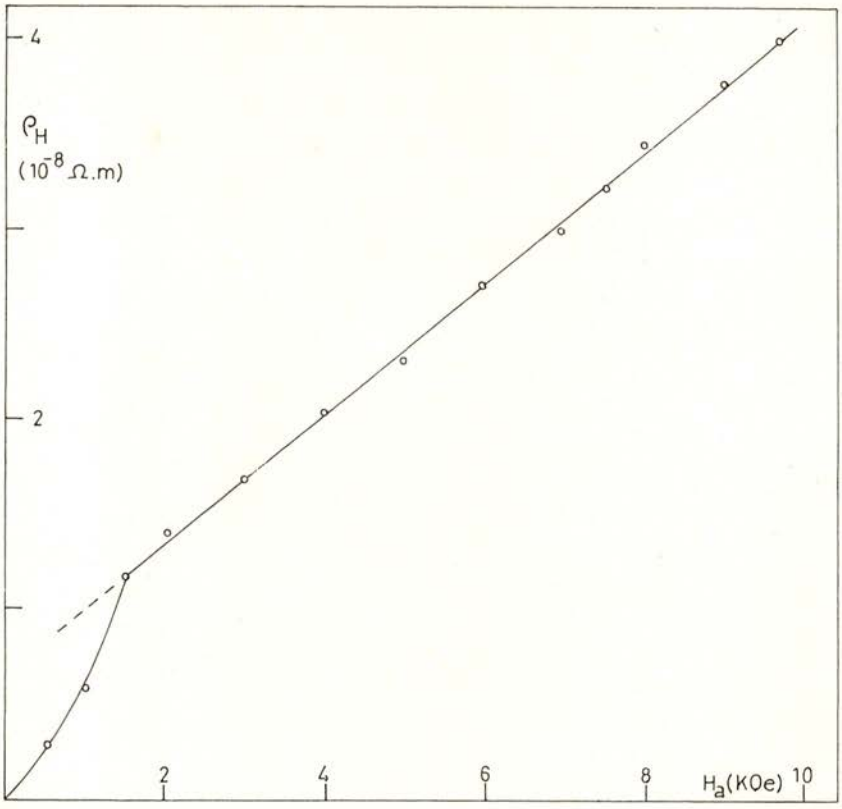

Fig. 7 — A plot of the Hall resistivity (ρ_H) versus the applied magnetic field for $HgCr_2Se_4$ at 77 K.

We consider now the Hall voltage measurements performed in the same $HgCr_2Se_4$ sample. As is well known, in an applied magnetic field (H_a) and for a magnetic single carrier semiconductor the Hall voltage is given by $V_H = (R_0 B + R_s \mu_0 M) I/d$, where R_0 is the ordinary Hall coefficient $R_0 = (ne)^{-1}$, n being the effective density of conduction electrons, B the magnetic field inside the sample, R_s the extraordinary Hall coefficient, M the magnetization, I the intensity of the electric current, d the thickness of the sample and μ_0 the magnetic permeability of vacuum [15]. In figure 7 we have a plot of the Hall resistivity

($\rho_H = V_H\ d/I$) as a function of the applied magnetic field when the sample is at 77 K. The onset of the saturation of the extraordinary Hall effect occurs for $B_d = 0.15$ Tesla. This is the typical behaviour for the magnetic field dependence of the Hall voltage in the spinel system. An order of magnitude of the free electron concentration (n) at 77 K can be calculated from the slope of the straight line of figure 6; its value is approximately 1.9×10^{19} cm^{-3} (the corresponding mobility for free electrons is 31 $cm^2\ V^{-1}\ s^{-1}$). That value agrees with 3×10^{19} cm^{-3} predicted for $T_c \simeq 124$ K from the law $T_c \propto n^{1/3}$ [4].

We have plotted the Hall resistivity (ρ_H) as a function of the temperature in figure 8, for an applied field of 0.97 Tesla.

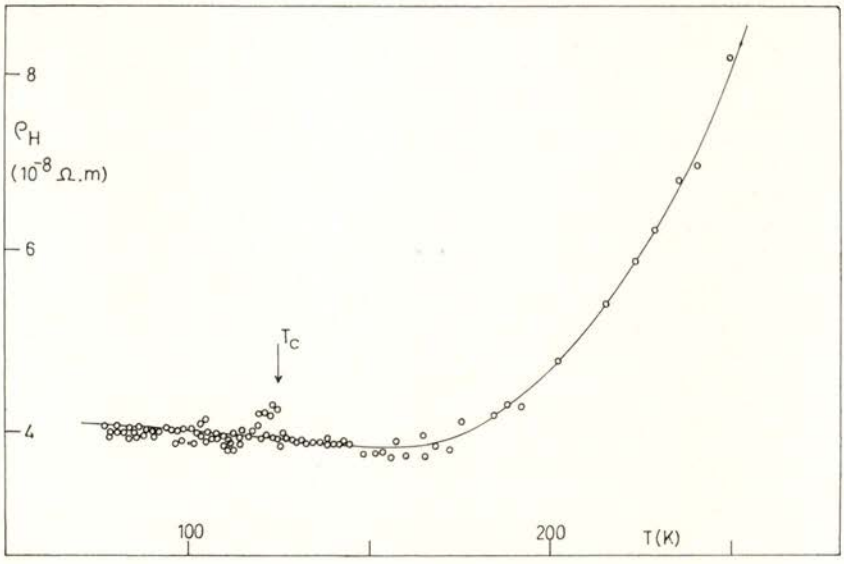

Fig. 8 — Temperature dependence of Hall resistivity (ρ_H) for $HgCr_2Se_4$ under an applied magnetic field of 0.97 Tesla.

ρ_H is approximately constant between 77 and 180 K and there is no significant anomaly around T_c, although appreciable 'noise' exists near this temperature. These instabilities can not be associated with experimental errors. A plot of ρ_H versus ρ

(figure 9) shows that above 160 K the Hall resistivity is proportional to ρ. This is due to the fact that in the higher temperature region the total Hall voltage is essentially equal to the ordinary voltage ($M(T) \simeq 0$) and according to the previous assumption, the mobility variation with the temperature is not relevant (at least for $T > 160$ K). For $T = 250$ K we obtain, $n = 8 \times 10^{17}$ cm^{-3} and $\mu = 28$ cm^{-2} V^{-1} s^{-1}, using the experimental values of R_0 and ρ, and the formulae $R_0 = 1/ne$, $\rho = R_0/\mu$.

Assuming, as before, that in all the temperature range studied mobility variation is much smaller than the variation of free

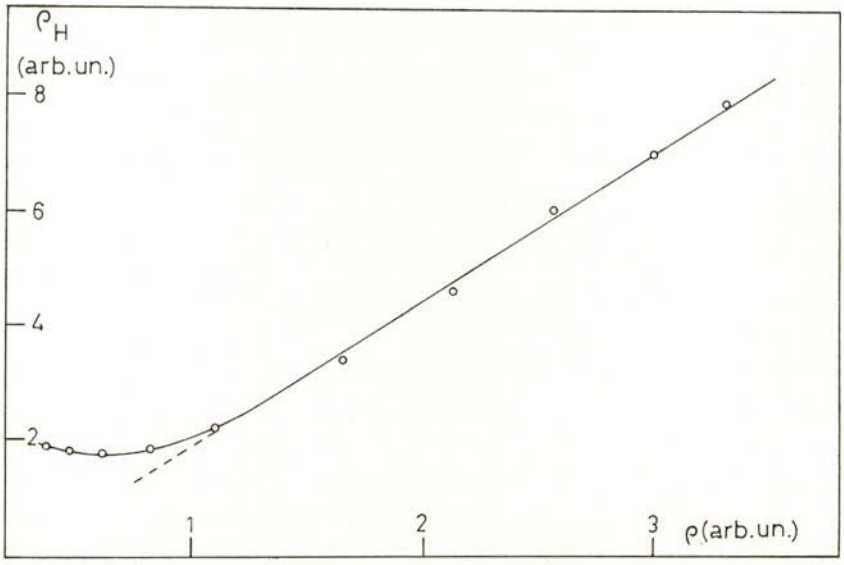

Fig. 9 — A plot of Hall resistivity (ρ_H) versus resistivity (ρ) for $HgCr_2Se_4$.

electron concentration [16], we have made a rough calculation to separate the extraordinary from the ordinary Hall resistivities. We have taken the ordinary Hall resistivity as proportional to the electrical resistivity; extraordinary Hall resistivity was derived by subtraction. The extraordinary Hall voltage as a function of

the temperature is shown in figure 10(a). An occasional cancellation of the ordinary and extraordinary Hall effects overshadows an anomalous behaviour of the sample around T_c. We have also used the law of variation of electron concentration with the

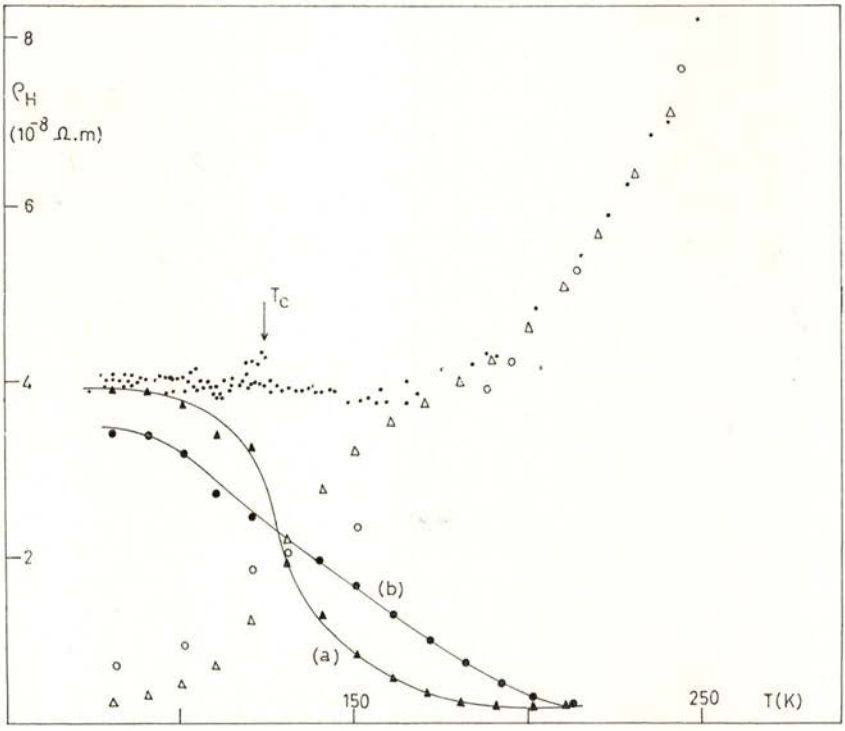

Fig. 10 — Temperature dependence of Hall resistivity (·); ordinary (Δ) and extraordinary (▲, curve a) Hall resistivities calculated from electrical resistivity and total Hall resistivity data; ordinary (o) and extraordinary (•, curve b) Hall resistivities from optical measurements.

temperature, determined by optical measurements in a n-type $HgCr_2Se_4$ [16], to separate the extraordinary and normal Hall resistivities. By using that law we derived the extraordinary Hall resistivity seen in figure 10(b). The results obtained are similar to

each other and clearly point to the existence of an appreciable magnetization in a large temperature range above T_c.

Fig. 11 displays the Seebeck coefficient (S) as a function of temperature for $HgCr_2Se_4$. It is negative in the whole temperature range studied, as expected, and $|S|$ increases as the temperature increases. $|S|$ is rather low and an order of magnitude smaller that the value reported for $CdCr_2Se_4$ [17]. The room temperature value we found agrees quite well with corre-

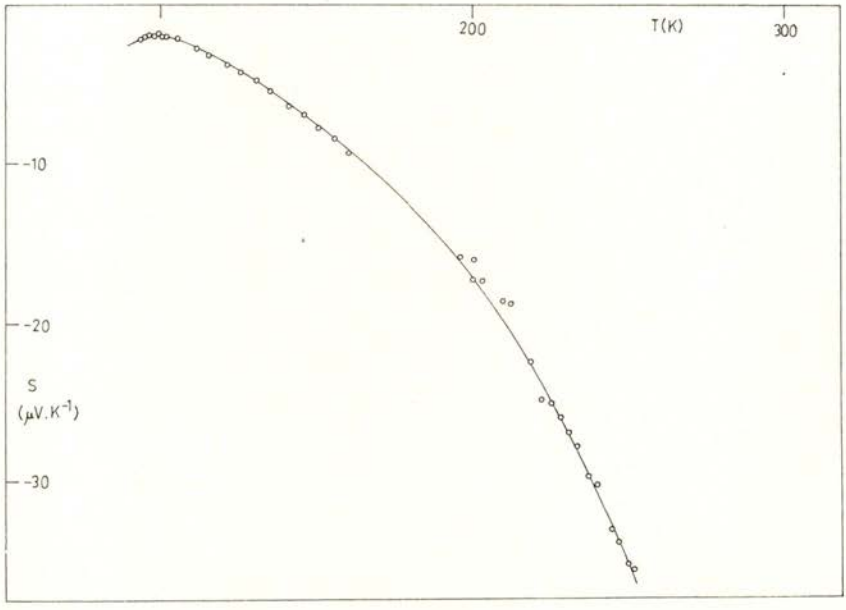

Fig. 11 — Seebeck effect (S) as a function of the temperature.

sponding values previously reported for $HgCr_2Se_4$ [2]. As we shall see, the values obtained for S can be well understood by assuming that, above 200 K, $HgCr_2Se_4$ is a semiconductor and below this temperature it behaves like a metallic system.

For a metallic system $S(T) = -(3/2 + q)\,\pi^2 k_B^2 T/(3\eta|e|)$, where η is the Fermi level and q is associated with the relaxation time [18]. As $\eta = (\hbar^2/2m)\,(3\pi^2 n)^{2/3}$ we have $\log n(T) = -3/2$

log $|S(T)|$ + const, by neglecting q. In figure 12 a plot of the experimental values of log ρ versus log $|S|$ gives a straight line, below 150 K, with a slope 1.6, approaching the theoretical value 1.5 (predicted in the above model) fairly well. Accordingly, for T = 150 K we have $\eta \simeq 0.5$ eV. Above 180 K, log ρ varies

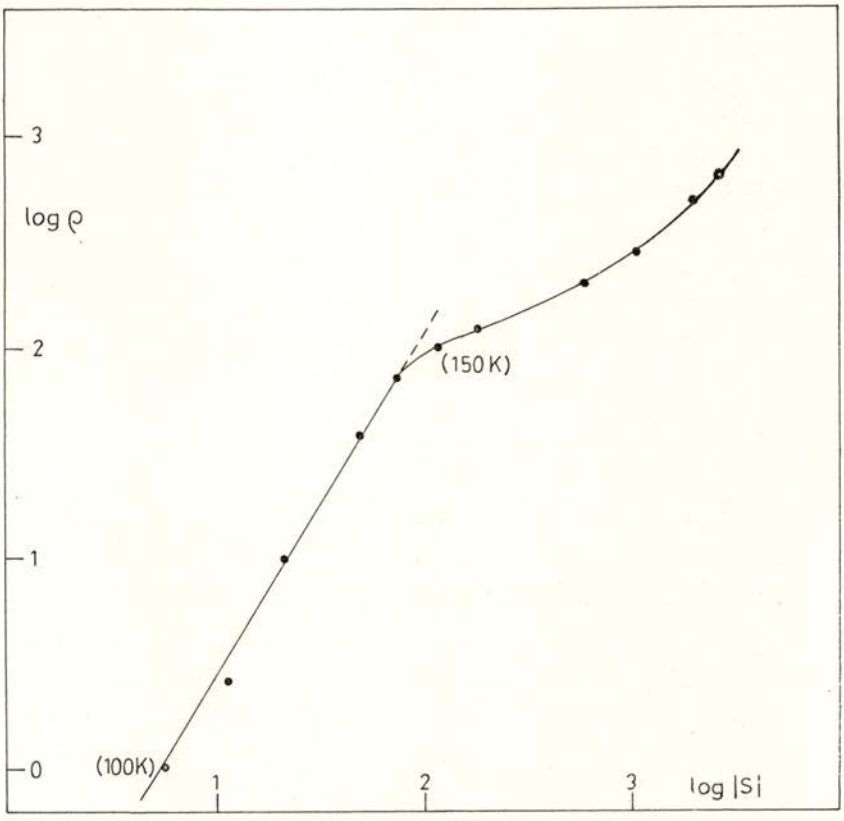

Fig. 12 — A plot of log ρ versus log $|S|$.

linearly with $|S|$ as we can see in figure 13. This is the result obtained from a simple model used in the study of a non-degenerate single carrier semiconductor with parabolic bands. In this case the Seebeck coefficient is given by [19]:

$$S(T) = -(k_B/|e|)\,|(5/2 + q) + \eta/(k_B T)| \qquad (1)$$

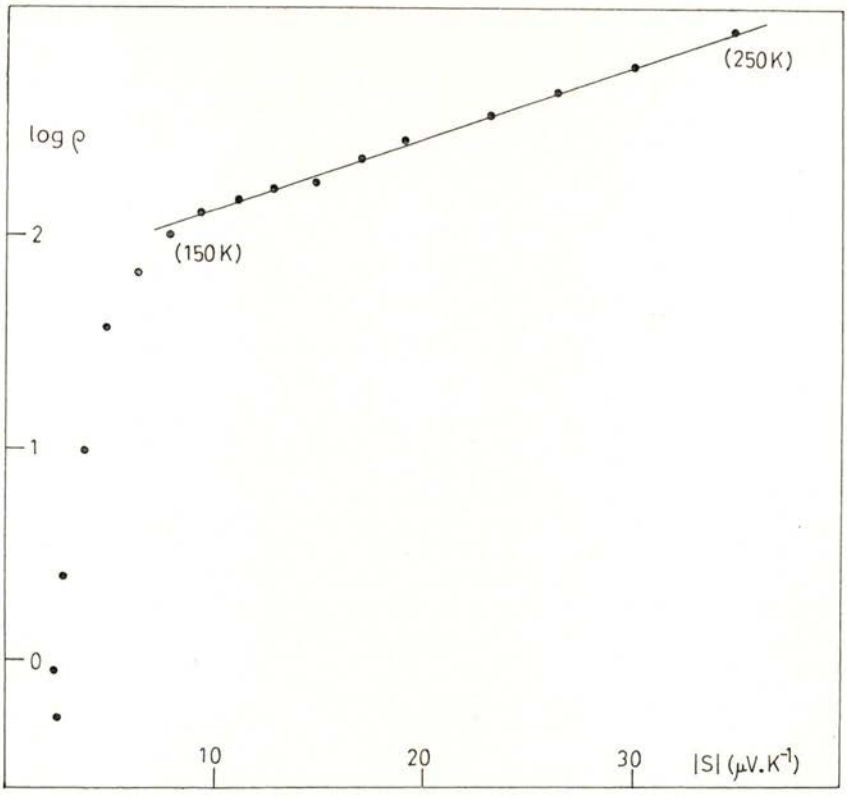

Fig. 13 — A plot of log ρ versus the Seebeck coefficient ($|S|$).

where $q = -1/2$ for acoustic mode scattering, while $q = 3/2$ for scattering by impurities. If $g(E)$ represents the state density for electrons and $f(E)$ the Fermi distribution

$$n(T) = \int_0^\infty g(E)\, f(E)\, dE = 4\pi\,(2m/\hbar^2)^{3}\sqrt{\pi/2}\,\exp(-\eta/k_B T) \tag{2}$$

Replacing (2) into (1) we have:

$$S(T) = -(k_B/|e|)\cdot|(5/2+q) - \log n(T) + \text{const}|$$

Using the assumption $\rho(T) \propto n(T)^{-1}$, we obtain

$$S(T) \simeq C \log \rho(T) + \text{const},$$

where C is constant.

It is quite interesting to remark that the variation of the Fermi level, which is associated with the Seebeck coefficient as we have just seen, follows the variation of the gap width (figure 14).

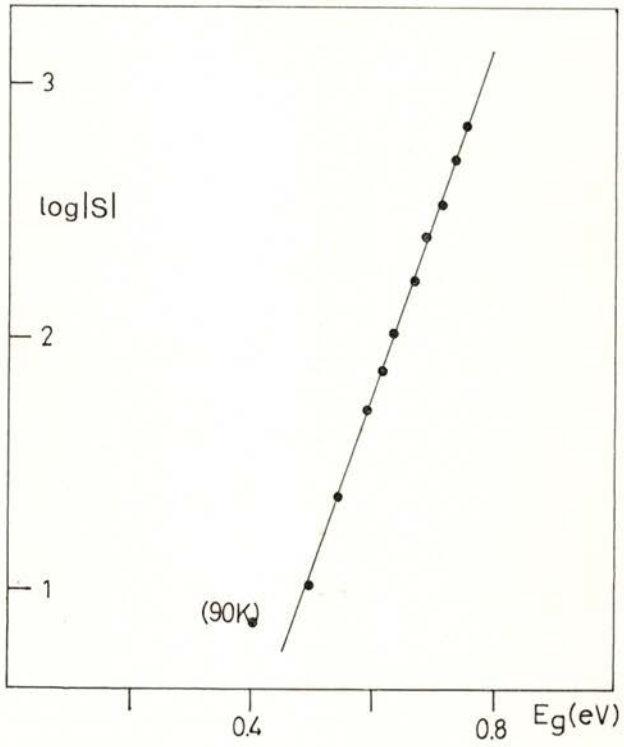

Fig. 14 — A plot of log | S | versus the gap width (E_g).

Log | S | versus E_g is a straight line between 90 and 200 K. The results concerning the Seebeck coefficient confirm the major importance of the electron concentration on the electrical properties of the n-type semiconductor $HgCr_2Se_4$. The small values of | S | may be explained by assuming that the Fermi level is very close to the bottom of the conduction band.

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