

THE PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 92, No. 2

OCTOBER, 15, 1953

Sensitive Hall Measurements on NaCl and on Photoconductive PbTe†

JOHN L. LEVY

Physics Department, University of Michigan, Ann Arbor, Michigan

(Received March 6, 1953; revised manuscript received July 6, 1953)

Sensitive Hall equipment was built according to a cross-modulation method with 60-cps magnetic field, 85-cps driving current, and 25-cps selective detection. An attempt was made to measure the Hall effect of ionic conduction in sodium chloride. Theoretically its Hall mobility is expected to be of the order of 10^{-7} m²/volt-sec (10^{-3} cm²/volt-sec). However, excessive current noise, of the order of 10 microvolt per cps, in the sample subjected to electric and magnetic fields of the order of 10^4 volt/m and 1 weber/m² at temperatures between 650°C and 800°C, prevented the observation of any Hall signal, yielding only an experimental upper limit of 10^{-7} m²/volt-sec (10^{-3} cm²/volt-sec) for the mobility.

Measurements of the Hall effect in photoconductive films of lead telluride at 30°C and -190°C are also reported. The results support Simpson's theory that the increase in photoconductivity is primarily due to an increase in carrier density and only secondarily to a change of mobility.

INTRODUCTION

WHILE the Hall effect for electronic conduction both in metals and semiconductors is measured relatively easily, the Hall effect of ionic conduction has never been detected. The main purpose for building the sensitive Hall apparatus described here was to detect the Hall effect for ionic conduction in alkali halides at elevated temperatures, near the melting point (about 800°C for sodium chloride).

The requirements for such an attempt were estimated as follows. The mobility of sodium ion vacancies in sodium chloride has been obtained by Etzel and Maurer¹ and ranges from 10^{-8} to 10^{-6} m²/volt-sec for the alkali halides in the structure-insensitive range of temperatures. This is about 10^{-3} times the lowest value of electronic mobilities in metals and semiconductors, which range from 10^{-5} to 2 m²/volt-sec. For an ionic crystal with linear dimensions of the order of 10^{-2} m, a magnetic field of the order of 1 weber/m², and an ionic mobility of 10^{-7} m²/volt-sec (or 10^{-3} cm²/volt-sec), the ratio of the Hall emf to the primary voltage is then of the order 10^{-7} and thus requires in conventional schemes of measurement the compensation of any

potential difference present between the Hall electrodes with a precision of one part in ten million with respect to the primary voltage. This difficulty can be avoided at the high temperatures used, only by certain ac methods. These also minimize effects of electrolytic polarization in the sample. We adopted the cross-modulation method used first by Russel and Wahlig.² Accordingly, we built equipment capable of measuring Hall mobilities of the order of 10^{-8} m²/volt-sec, provided the noise generated by the sample is not excessive.

In addition to the primary purpose, the equipment was also used for the measurement of the Hall effect of photoconducting films of lead telluride. Since Hall mobility values were available only for the bulk material which is not photoconductive, the values for thin films should provide significant information regarding the mechanism of photoconductivity in such materials. According to Simpson's³ theory the photoconductivity in lead telluride films results essentially from an increased density of carriers, excited into the conduction band by the incident radiation. The carrier mobility is assumed to be a slowly varying function of temperature and irradiation. We intended to verify this assumption experimentally by measuring the Hall mobility at room temperature and as a function of the irradiation at liquid air temperature.

† Supported by the U. S. Office of Naval Research. Part of a dissertation submitted to the University of Michigan for the degree of Doctor of Philosophy.

¹ H. W. Etzel and R. J. Maurer, *J. Chem. Phys.* **18**, 1003 (1950).

² B. R. Russel and C. Wahlig, *Rev. Sci. Instr.* **21**, 1028 (1950).

³ O. Simpson, *Trans. Roy. Soc. (London)* **A243**, 578 (1951).

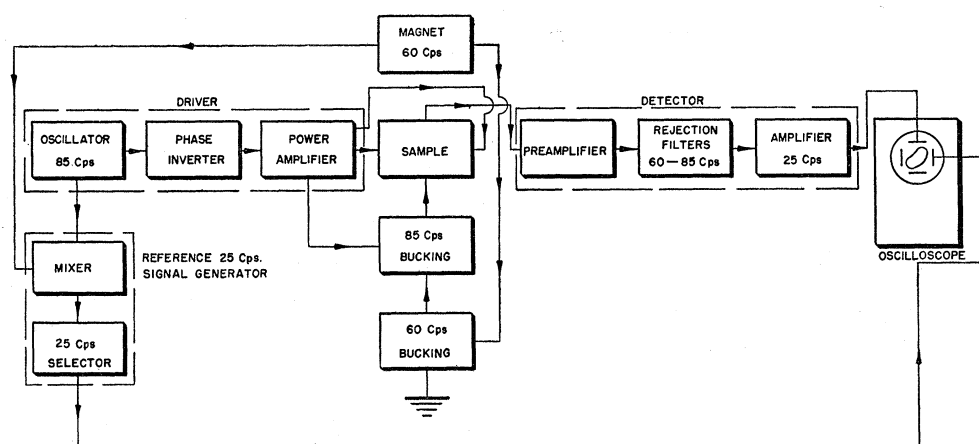


FIG. 1. Block diagram of the apparatus.

APPARATUS

a. Electronic Apparatus and Magnet

The apparatus, designed according to a cross-modulation method similar to that of Russell and Wahlig,² is represented by the block diagram in Fig. 1.

The driver, producing the 85-cps primary electric field applied to the sample, is capable of delivering 20 watts with negligible distortion, and its output can be matched to the sample impedance within a large range. In order to avoid spurious mixing of 85-cps and 60-cps signals, for instance through 60-cps magnetic pickup by transformers, R - C coupling and R - C filters in feedback circuits were used exclusively.

The laminated silicon steel magnet produced a 60-cps alternating field, essentially uniform within a 3×6 cm area. The ellipse of $0.95B_{\max}$ has axes of 3.4 and 5.4 cm. The air gap width was 3.5 cm. The maximum peak field produced without distortion was about 1.5 weber/m². The power requirements of the magnet made the choice of 60 cps almost imperative.

The Hall signal was measured at the difference frequency of 25 cps. This frequency was chosen as a compromise between various tendencies. The high-input impedance required by the samples favored a low frequency. The frequency drift in the line voltage and a reasonable response time, combined with a good signal-to-noise ratio favored a not too low frequency. Finally, a frequency that could not be produced by combinations of overtones of the magnet and driver frequencies was desirable. These and other considerations led to the adopting of the frequencies of 60, 85, and 25 cps.

The Hall signal was amplified by the detector. Its sensitivity and bandwidth were about 1 microvolt and 1 cps, respectively. The selective part of the detector could also be tuned to 60 cps or 85 cps to guide and check the balancing out of the corresponding voltages in the Hall-probes circuit. For this purpose, two bucking sections provided signals of 60 and 85 cps, adjustable with a relative precision of 10^{-4} . In each section a Helipot potential divider provided the amplitude ad-

justment, while the phase was set by a sine-cosine resolver loaded with a suitable R - C circuit. All sensitive parts of the detector were carefully shielded against electric, magnetic, and mechanical disturbances.

The Hall mobility sign was determined by observing on an oscilloscope the phase of the detector output relative to a reference signal. The calibration of the apparatus was checked by measuring the Hall mobility of a Ge sample, kindly measured independently and put at our disposal by W. C. Dunlap of the General Electric Research Laboratory.

b. Sample Holders and Samples

For the measurements on sodium chloride which were taken between 650°C and 800°C, $2.5 \times 20 \times 20$ mm synthetic optical grade single crystal samples of high purity, manufactured by the Harshaw Chemical Company, were placed in a lavite oven, shaped like a cigar box with two dc heating coils imbedded in the large faces. Approximately 400 watts, derived from storage batteries, were required to heat the box to the melting point of sodium chloride. The temperature of the sample was monitored by a chromel-alumel thermocouple, whose emf was calibrated in situ against melting points of several alkali halides in this temperature range. It was found that the most accurate and convenient determination of the sample temperature was by measurement of its electric conductivity.

The current electrodes consisted of 0.001-inch thick platinum foils pressed against the crystal by an assembly of quartz rods, plates, and springs. We observed no improvement in the electrical behavior of the sample when a platinum film was first deposited on the electrode areas of the sample by applying a coat of "liquid bright platinum." The Hall electrodes were made with 2×2 mm tongues of the same material. The ends of the quartz rods pressing them against the crystal were shaped into 1×2 mm rectangular areas, so that the Hall electrodes had approximately the same extension. After the crystal had been kept above 700°C

for a few minutes, the platinum foils adhered firmly to the sample.

For the measurements on lead telluride films, which were taken at 30°C and under controlled illumination at -190°C, photoconductive cells were especially prepared. The graphite electrodes were first painted on the Pyrex support of the cell with a coat of Aquadag. The distance between primary electrodes was about 10 mm, while the Hall electrodes were 1 mm apart. The cell envelope was then sealed to a vacuum system and the films were deposited according to Simpson's evaporation procedure.³ The finished cell was placed in a light shielded cryostat. A glass tube sealed to the cell served as a light pipe to bring controlled amounts of irradiation onto the film from a light source outside the cryostat.

The results scattered, partly because the current noise between Hall probes was an appreciable fraction of the Hall signal at liquid air temperature, and partly because the cells were not stable, i.e., did not exhibit a definite and reproducible resistance when kept at -190°C under constant illumination. However, the measurements still permitted drawing significant conclusions.

RESULTS AND CONCLUSION FOR SODIUM CHLORIDE

A number of measurements were taken for various samples of sodium chloride at $B=0.86$ weber/m² rms. Excessive current noise of about 10 microvolt per cps in the sample when subjected to the electric and magnetic fields prevented the detection of any Hall emf. Consequently, only an experimental upper limit for the Hall mobility could be determined. The results are summarized in Table I.

The primary voltage of about 200 volts represented an electric field of 10⁴ volt/m. The primary current ranged between 1.6 and 26 milliamperes, generally increasing with higher temperature T , which ran from 650°C to 795°C, as determined from the conductivity. The resulting rms noise V across the Hall electrodes in microvolts set a lower limit to the mobility that could be measured, or an upper limit μ_{\max} for mobilities that escape measurement. This upper limit for the Hall mobility was of the order of 10⁻⁷ m²/volt-sec.

Since electrons are expected to exhibit a considerably higher mobility, this suggests that, even near the melting point, no appreciable electronic conduction takes place. Furthermore, this experimental limit does not conflict with the estimates of the difference between mobilities of positive and negative vacancies that can be derived from Etzel's data on the mobility of sodium vacancies¹ and on Tubandt's measurements of transport numbers⁴ at lower temperatures. This estimate was obtained as follows. According to Etzel the mobility of positive carriers is given by

$$\mu_+ = (1.96/T)e^{-9860/T} \text{ m}^2/\text{volt-sec.}$$

⁴C. Tubandt, *Handbuch der Experimental Physik* (Julius Springer, Berlin, 1932), Vol. 12, p. 402.

For the algebraic sum of the mobilities we have

$$\mu_+ - |\mu_-| = \mu_+(1-r),$$

where

$$r = |\mu_-/\mu_+|.$$

The temperature dependence of μ_- is assumed to have the same forms as μ_+ . Thus, r has the form:

$$r = Ae^{-B/T}.$$

Since only Schottky defects are assumed to be present in NaCl, the densities of carriers of opposite sign are equal, and r equals the ratio of the transference numbers. Thus, Tubandt's data can be used to find the constants A and B , and this leads to

$$r = 1900e^{-9100/T}.$$

Tubandt's data lie in the range of 560-625°C. The constants A and B are assumed to be unchanged up to the temperature range of our experiments (650-800°C). The over-all rms error in $\mu_+ - |\mu_-|$ was estimated and was found to be 10 percent. The resulting values for $\mu_+ - |\mu_-|$ were 0.45×10⁻⁷ m²/volt-sec at 650°C and 1.3×10⁻⁷ m²/volt-sec at 795°C. These are seen to be of the same order of magnitude as the limit set by the noise.

While the precise cause of this noise is at present not known, the following information may be helpful in its interpretation. The noise is definitely a current noise and is more than a factor of 10 higher than the Johnson noise of the crystal and the entire detecting system combined. It is proportional to the crystal current and independent of the magnetic field. The values given are obtained after a few minutes of current; immediately after the current is switched on the noise is greater. The noise may have been connected with some plastic deformation in the crystal near the Hall electrodes. This deformation could not be avoided at the high temperatures used, without causing a poor contact between electrodes and crystal. Sufficient tests have been

TABLE I. Measurements on single crystals of sodium chloride.

V_A^a volt	I_A ma	V microvolt	$\sigma \times 10^{-6}$ ohm ⁻¹ cm ⁻¹	T °C	$\mu_{\max} \times 10^7$ m ² /volt-sec
240	1.6	31	2.7	650	3
240	1.6	7.5	2.7	650	0.8
240	3.4	12.5	5.7	680	1.3
240	5.4	11	9	705	1.1
225	11.7	10	21	745	1.3
270	21	7.5	31	765	0.68
175	15	22.5	34	770	3.1
240	21	10	35	775	1
220	19	15	35	775	1.7
240	21	10	35	775	1
240	26	14	43	785	1.4
220	25	10	45	785	1.1
200	22	4.5	44	785	0.55
180	22	8.5	49	795	1.2

^a V_A = primary voltage; I_A = primary current; V = rms noise between Hall electrodes; σ = conductivity of sample; T = temperature; and μ_{\max} = experimental upper limit of Hall mobility (1 m²/volt-sec = 10⁴ cm²/volt-sec).

TABLE II. Measurements of the Hall effect in a photoconductive lead telluride film.

B^a weber/ m ²	V_A volt	$V \times 10^4$ volt	$R_p \times 10^{-5}$ ohm	$R_H \times 10^{-4}$ ohm	$\mu \times 10^4$ m ² /volt- sec	T °C	Remarks
0.43	24.5	11.8	2	6.2	1.5	30	
0.22	24.5	5.25			1.34	30	
0.22	102	25			1.53	30	
0.43	100	43.8			1.37	30	
0.43	150	69			1.44	30	
0.22	150	35			1.46	30	
			>10 ⁴ 5000	>10 ⁴ 2800		-190	dark
0.43	100	37.5			1.17	30	illuminated
0.65	100	56.1	1.9	6	1.17	30	
0.65	24.5	10.6			0.9	30	
0.43	24.5	9			1.15	30	
0.43	12	5			1.3	30	
0.32	11.5	5	1.7	5	1.8	30	
0.32	19.5	6.25			1.34	30	
0.32	234	1		2000	1.78	-190	dark
0.32	210	37.5		800	1.12	-190	illuminated ^b
0.65	210	62.5		800	0.93	-190	illuminated ^b
0.32	195	62.5		5	1.33	30	
0.43	234	31	9	17	4.1	30	cell leaks

^a B = rms magnetic field, V_A = primary voltage, V = Hall signal, R_p = sample resistance between primary electrodes, R_H = sample resistance between Hall electrodes, μ = Hall mobility (1 m²/volt-sec = 10⁴ cm²/volt-sec), and T = temperature of the sample.

^b Rms input noise 2.10⁻³ volt at 25 cps.

made to ascertain that the noise originates in the crystal. Its spectrum has not been determined. Investigations aimed at lowering the noise level are being carried on.

RESULTS AND CONCLUSIONS FOR LEAD TELLURIDE FILMS

A typical series of consecutive measurements on a lead-excess film is presented in Table II. The film was N type, as determined by the sign of its thermoelectric power, measured between primary electrodes. The sample conductivity, measured both between primary and between Hall electrodes depended on aging and thermal history of the cell. Also it drifted appreciably during illumination. The noise level between Hall electrodes was in general an appreciable fraction of the Hall signal. Nevertheless, examination of Table III, in which the average values of measurements on a group of five cells are presented, brings out the following features of physical interest.

(a) The Hall mobility at room temperature is of the order of 10⁻⁴ m²/volt-sec if the cell is photoconductive at low temperature; and its sign is the same as that of the thermoelectric power. It is positive for tellurium excess and negative for lead excess cells.

(b) At liquid air temperature the Hall mobility is of the order of 10⁻⁵ m²/volt-sec, whether the film is irradiated or not. At the most it changes by a factor of

two, while the conductivity changes by a factor up to 25. Its sign is the same as at room temperature.

The order of magnitude of the Hall mobility in our samples is the same as in PbS and PbSe cells used by Lothrop⁵ and Halvorsen.⁶ This suggests that our films might have been activated by traces of oxygen, which were absent in Simpson's samples.

Since the Hall mobility change was small compared to the concurrent conductivity change, the increase in carrier density seemed to be mainly responsible for the photoconductivity, as was assumed by Simpson.

On the other hand, the Hall mobility in our films was much smaller than in the bulk material.⁷ This could be

TABLE III. Summary of measurements on films of lead telluride.^a

Cell	T °C	R_H kilo- ohms	R_p kilo- ohms	$\mu \times 10^4$ m ² /volt-sec	Remarks
1	25	12	32	+21.5	Te-excess, P -type, large drift
1	-190	60	270	+2.2	dark
1	-190	59	240	+1.9	light
2	25	1.8	2.2	-104	large Pb-excess, N -type
2	-190	1.5	1.6	-124	no photo conductivity
3	30	50	200	-1.28	Pb-excess, N -type, small drift
3	-190	20 000	>10 ⁶	-1.78	dark
3	-190	8000		-1.12	light
4	30	20	53	-2	Pb-excess, N -type, large change after first cooling
4	-190	5000		+0.07	dark
4	-190	50		+0.15	light
5	30	40	100	-1.4	Pb-excess, N -type
5	-190	10 000	>10 ⁶	-2	dark
5	-190	1200	2300	-1.5	light

^a Symbols as in Table II.

explained by the presence of potential barriers in the films or by the granular structure of such evaporated layers.

ACKNOWLEDGMENTS

We wish to thank Dr. E. Katz for suggesting the problem and for his guidance during the research, R. W. Terhune for the preparation of the cells used in the experiments, A. G. Dockrill for technical assistance, and Dr. W. C. Dunlap of the General Electric Company for furnishing a calibrated sample of Ge.

⁵ E. W. Lothrop, Jr., Thesis, Northwestern University, 1949 (unpublished).

⁶ K. G. Halvorsen, Thesis, Northwestern University, 1951 (unpublished).

⁷ R. P. Chasmar and E. H. Putley, Conference on semiconducting materials, University of Reading, 1950 (unpublished).