Microwave Hall effect measurements on biological and organic semiconductors

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Abstract. Microwave Hall effect measurements have been performed by improved 10 GHz bimodal cavity resonators with hybrid end walls used to avoid the background signal that obscures the measurements on low mobility materials. Hall mobility results on copper phthalocyanines CuPc and other organic semiconductors, in the range of 8 cm²/Vs to 60 cm²/Vs, provide evidence of acoustic phonon scattering as the dominant conduction mechanism. Presently, the microwave Hall effect seems to represent the only means available for quantitative measurements on biological substances like DNA and proteins, which yield mobility values lower than 10 cm²/Vs, and are therefore consistent with conduction mechanism involving hopping of charge carriers between localized energy sites.

1. Introduction

The microwave Hall effect technique (MHE) remains one of the most valuable tools for characterization of semiconductors. Its recent utilization for high magnetic field measurements in high mobility two dimensional electron gas GaAs samples, fine magnetic particles, ZnO powders and photo-cells [1-4] has widened its scope of application despite the technique’s unpopularity due to its tedious, cumbersome and laborious tuning, calibration and experimental procedures. However, the main area of attraction for the implementation of the MHE technique is low-mobility measurements, particularly on biological, polymers and organic substances where macroscopic defects such as electrode contacts, space charges, and intercrystalline and intracrystalline defects can seriously influence the results [5-8]. At microwave frequencies, the Hall effect occurs as Faraday-type rotation in the plane of polarization of the microwaves as they pass through the sample. This rotation may be amplified by placing the sample in a high-Q cavity resonator with a degenerate-mode configuration.

In this paper, measurements on a number of biological and organic materials using microwave bimodal cavity resonators of a rectangular geometry operating at its fundamental modes or cylindrical one operating at the TE11p degenerate modes are presented and Hall mobility values are reported.

2. Measurement Technique

In MHE, measurement on low-mobility and high-resistivity materials is performed by placing the sample at the centre of the bimodal cavity resonator and applying a static magnetic field B which produces a Hall effect in the sample and causes the output mode to couple to the input one. The Hall mobility of the sample may be expressed by [1]:
\[ \mu_{11} \approx \frac{1}{B} \frac{|S_{21}|}{(1 - S_{11}) \left(1 - \frac{Q}{Q_0}\right)} \]  

where \( S_{21} \) is the cavity transmission coefficient representing the Hall output power, \( S_{11} \) the cavity reflection coefficient, \( Q_0 \) and \( Q_1 \) are cavity loaded Q-factor before and after the application of \( B \).

However, an empty cavity will still produce a signal due to the Hall effect in its metal end walls. This signal may be comparable to the signal generated by the sample, and is described by the elements of the S-matrix [9-10]:

\[ |S_{21}| = \mu_{\text{Hew}} \frac{B}{R} \left(1 - S_{11}\right) \left(1 - S_{22}\right) \]  

where \( \mu_{\text{Hew}} \) is the Hall mobility of the end-wall material, and \( R \) is a cavity geometry factor given by [9-10]:

\[ R = k \left[ 2 + \left(\frac{d}{a}\right)^{\frac{3}{2}} + \left(\frac{d}{a}\right)^{\frac{2}{3}} \right] \]

where \( a \) is the radius of a cylindrical cavity operating at the TE\(_{11p}\) mode, or the size of the cross-sectional area for a rectangular cavity operating at its fundamental TE\(_{101}\) and TE\(_{011}\) modes, \( d \) is the length of the cavity, and \( k \) is a constant equals to \( \frac{\mu}{8} \) for the cylindrical cavity and \( \pi/8 \) for the rectangular one.

The microwave measurement system, shown in figure 1, consists of a bimodal cavity resonator, excited in two degenerate and orthogonal modes operating at 10 GHz. A number of X-band cylindrical and rectangular cavities were used, with a Q-factor of up to 6000, and with removable copper end walls plated with 2 µm cadmium layer in order to form a hybrid metal so as to minimize the effects of the empty cavity Hall signal which can be comparable or even higher than that generated by the Hall effect in the low-mobility semiconductors studied in this work. The measurement system utilizes either a microwave vector network analyzer, e.g. of the type HP8720A, or a less expensive superheterodyne receiver. Details of the experimental apparatus can be found elsewhere [1-2, 11-12].

![Figure 1. Schematic of the microwave Hall effect system:](image)

(1) microwave generation and detection, (2) isolator, (3) directional coupler, (4) attenuator, (5) phase shifter, (6) cavity.

3. Results and Discussion

The use of MHE for the study of biological substances and organic semiconductors has long been inspired by Eley whose pioneering work in this field resulted in the first experimental evidence for electronic semiconduction in crystalline organic solids as early as 1948. He was also the first to
suggest the existence of energy bands in biological systems and laid down the ground to the theory that the observed semi conduction was associated with the overlapping between molecules of π-electron atomic orbitals. Consequently, attempts to understand the physical basis for the existence of energy bands in biological systems were approached from the knowledge gained in the more established field of organic semiconductors [5]. Serious work to study organic biological materials were then made in 1970 and onwards using the MHE technique and attempts to reproduce some of the results is presented using the improved measurement system.

In this work, room temperature Hall effect measurements were initially carried out on copper phthalocyanine CuPc(B) monomer which yielded a p-type mobility value of 40 cm²/Vs as shown table 1. This firmly puts the mechanism of transport in the band model domain. The dependence of mobility in temperature was also investigated and determined from a least square fit to be T⁻¹.². Similar results were obtained for CuPc(CN)₈ giving a p-type mobility of 23 cm²/Vs with an approximate temperature dependence of T⁻⁰.¹. This behaviour was difficult to explain as lattice phonon scattering should dominate at higher temperature giving at least T⁻¹ dependence. Because the magnitude of the measured mobility was above 10 cm²/Vs, the localized carrier model could not be used to explain the observed behaviour. However, the disordered nature of the material might account for the anomalous behaviour of the Hall mobility [13]. In addition, the measured n-type microwave Hall mobility for Lithium phthalocyanine LiPc of 60 cm²/Vs and Nickel phthalocyanine NiPc of 32 cm²/Vs which are in agreement with the result obtained for CuPc, but in contrast with what is usually expected for organic semiconductor. Finally, measurement on aluminum flouro phthalocyanine PcAlF yielded an n-type value of 8 cm²/Vs which is very low compared with CuPc [13].

Table 1. Microwave Hall effect mobilities of DNA and biopolymers.

| Material                  | Mobility µ_H in cm²/Vs. | Polarity |
|---------------------------|--------------------------|----------|
| CuPc                      | 40                       | p        |
| CuPc(CN)₈                 | 23                       | p        |
| LiPc                      | 60                       | n        |
| NiPc                      | 32                       | n        |
| PcAlF                     | 08                       | p        |
| DNA < dry                 | 01                       | n        |
| 50% hydration             | 08                       | n        |
| Collagen-MG complex       | 06                       | p        |
| Collagen                  | 02                       | n        |
| Bovine Serum albumin      | 02                       | n        |

For biological material, mobility results on dry and hydrated DNA yielded different values which indicate that there is a transition of conduction dominant carriers between n-type into p-type while going from dry to hydrated form. Moreover, the polarity of the dominant charge carriers also changes and depends on the level of hydration. This difference between dry and hydrated specimens has been attributed to the fact that dry DNA is considered as an intrinsic conductor in which electrons may be transferred between the nitrogen bases and the sugar-phosphate chain [6-8]. Mobile holes will then be able to move across the planes of the stacked bases as a consequence of increasing the hydration. Thus, hydration in DNA may give rise to an increase in the intermolecular and intramolecular hydrogen-bond network which results in providing a conduction band for long-range movement of free electrons. It should be however emphasized that these microwave measurements were made at the extreme level of system detection capabilities where it may be difficult to distinguish between the Hall signal generated by the sample and that of the cavity end walls. The reduction of the Hall mobility with increasing hydration may also be attributed to the overestimation of the large dielectric losses associated with loosely bound water. Rotations associated with free radicals or bound donor/acceptor
sites can also affect the measurements where the Hall effect may dominate the observed microwave rotation [6-8].

The Hall mobility of other biological protein and polypeptide samples was measured such as collagen-MG complex which yielded a p-type mobility of 6 cm²/Vs. This may indicate that the conduction mechanism in this material is due to band conduction where methylglyoxal can act as an electron acceptor when incorporated into protein structures [6-8]. However, other substances gave low-mobility results which should be treated with caution, again because of the detection sensitivity of the system. Most of these values may however suggest a hopping conduction mechanism if a more efficient technique to eliminate the empty cavity signal is implemented such that credible and reproducible measurement can be made without driving the detection system into its extreme limits.

4. Conclusions

Microwave Hall mobility measurements on biological materials seem to indicate that the most probable mode of conduction mechanism may involve hopping between localized states. Hydration in DNA may also results in providing a conduction band for long-range movement of free electrons and the possibility of electronic charge transport in bands of extended states. On the other hand, measurements on organic semiconductors indicate that the conduction mechanism is due to acoustic phonon scattering. Many of the Hall mobility results have however been obtained with a measurement technique operating near the limit of its sensitivity and several theoretical and practical complications regarding the interpretation of the observed Hall-type signal need to be resolved. One important approach is to make measurement at frequencies beyond 30 GHz in order to reduce the end walls size and the cavity geometry coefficient and consequently the empty cavity signal which is the main source of noise that affects the accuracy of measurements.

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