

Electron-molecule collision ionization in hydrogen and deuterium

I R Cowling and J Fletcher

School of Physical Sciences, Flinders University, Adelaide, 5042, Australia

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Abstract. The ionization of a gas molecule has been experimentally studied by measurement of both the electron-molecule ionization cross section in an electron beam, Q_i , and the electron ionization coefficient of an electron swarm, α/N . The results are presented for both hydrogen and deuterium and a comparison of the theoretical values of α/N , calculated from the present values of Q_i using various electron energy distribution functions, $F(\epsilon)$, with the present experimental values of α/N in hydrogen, indicates which form of $F(\epsilon)$ is most probable in this gas.

1. Introduction

The ionization of gas atoms and molecules by the direct impact of an electron may be studied either by directing a mono-energetic beam of electrons onto a gas target and measuring the ions produced, or by the amplification of an electron swarm moving through the gas in the presence of an electric field, E . The former method gives the ionization cross section Q_i while the latter method yields the first Townsend ionization coefficient, α/N , where α is the number of ionizing collisions per electron per centimeter of path in the field direction and N is the number density of the gas particles.

The absolute ionization cross sections in hydrogen have been measured, over an extended range of incident electron energy, ϵ , by only Tate and Smith (1932), Rapp and Englander-Golden (1965) and Harrison (1956). Data from the first two determinations disagree by up to 5% while the latter is approximately 40% higher at the peak of the Q_i against ϵ curve. In deuterium the only measurements for $\epsilon < 500$ eV are those of Rapp and Englander-Golden (1965). The technique involved is apparently simple. A gas target, in a field free region, is bombarded by a beam of mono-energetic electrons at energy ϵ , and the ions produced are drawn off and measured. The ratio of the resulting currents

$$I_i(\epsilon)/I_e(\epsilon) = NLQ_i(\epsilon) \quad (1)$$

where N is the number density of the gas, L is the length of the electron trajectory through the collision region, Q_i is the total ionization cross section.

The ionization coefficient has been subject to far more intensive investigation. The growth of current through a gas is given by the Townsend relationship

$$I = \frac{I_0 \exp\{(\alpha/N)Nd\}}{1 - (\omega/\alpha) \exp[\{(\alpha/N)Nd\} - 1]} \quad (2)$$

where I_0 is the initial (photoelectron) current from the cathode, α/N is the primary ionization coefficient and ω/α the secondary ionization coefficient and d is the inter-electrode gap separation. Data of I as a function of d at a constant E/N may be analysed by a three point analysis as by Jones and Llewellyn-Jones (1958) and Davies and Milne (1959) or by the Gosseries method (Haydon and Robertson 1961), to give values of α/N . Despite the several attempts to measure α/N as a function of E/N agreement is far from satisfactory even in hydrogen, the most frequently investigated gas. To date three sets of results in hydrogen appear to be equally valid; those of Jones and Llewellyn-Jones (1958), Fletcher and Davies (1963) and Haydon and Stock (1966). The only published data available for deuterium are those of Rose (1956) and Davies (1961). However it has long been considered that Rose's results are too high since he did not allow for secondary effects. It should be noted that Chanin and Rork (1963) take issue with this objection.

The relationship between $Q_i(\epsilon)$ and α/N is of great interest since they are related through the electron energy distribution function $F(\epsilon)$;

$$\frac{\alpha}{N} = \left(\frac{2e}{300m} \right)^{1/2} (N\mu)^{-1} (E/N)^{-1} \int_{\epsilon_i}^{\infty} \epsilon^{1/2} Q_i(\epsilon) F(\epsilon) d\epsilon \quad (3)$$

where μ is the electron mobility and ϵ_i is the ionization energy of the molecule. Knowledge of $F(\epsilon)$ enables other transport parameters, such as the diffusion coefficient and mean electron energy, to be calculated. It is thus the aim of the present work to measure both $Q_i(\epsilon)$ as a function of ϵ and α/N as a function of E/N with the intention of using the data to determine which published values of $F(\epsilon)$, both experimental and theoretical, must be used in equation (3).

2. Experimental details

The apparatus consists of two main parts, a chamber in which ionization cross sections are measured and a chamber in which ionization by electron swarms is investigated. These chambers are connected to a manifold on which is included an ion pump for the final stage of evacuation and an MS 10 mass spectrometer for analysis of both the residual gases after evacuation and the experimental gases used. The manifold, chambers and gauges are baked at 210°C for an extended period. Initial evacuation is performed by a conventional, well trapped, vacuum system which attains a base pressure of $<10^{-7}$ Torr. The ion pump then gives a final base pressure of $\sim 10^{-9}$ Torr in the ionization chambers. Gas pressures in the chambers are measured using an AEI VH 20 ion gauge for $p < 10^{-3}$ Torr and an NRC Alphatron gauge for $p > 10^{-4}$ Torr. Both these gauges are calibrated, *in situ*, against an MKS Baratron secondary standard, the lower pressures by a successive expansion technique, giving an error of $\pm 0.5\%$ in the Alphatron gauge and $\pm 2\%$ in the ion gauge, most of this latter error being in the measurement of the ratio of the volumes rather than error in the Baratron. The Baratron calibration was checked against an oil manometer and found to be accurate to within $\pm 0.2\%$.

The gases considered in the present experiments, hydrogen and deuterium, were purified by being admitted to the system through a palladium-silver alloy osmosis tube. Mass spectrometer readings indicate that the partial pressure of all impurities is of the order of 10^{-9} Torr when the gas pressure is 10^{-5} Torr, the operating pressure range for the ionization cross section measurement.

2.1. Ionization cross-section chamber

A schematic diagram of the chamber used for measuring ionization cross sections is given in figure 1. It consists essentially of three sections, the electron gun, the collision region and the electron collector. The electrons are released from an oxide-coated

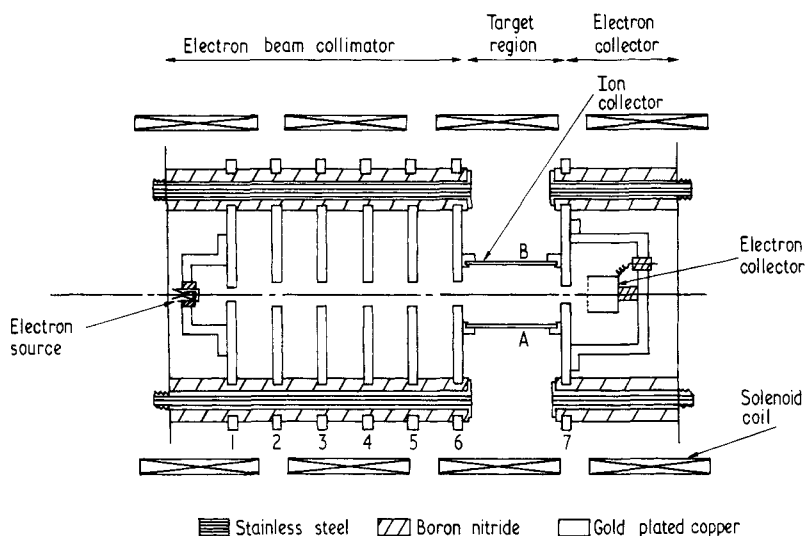


Figure 1. Schematic of the ionization cross section chamber.

cathode, and are, in the present experiments, uniformly accelerated through a 2 mm aperture in plate 1 and 5 mm apertures in plates 2 to 6. The collision region, bounded by plates 6 and 7, the ion pusher plate A and the ion collector plate B, is 3.0 cms long in the axial direction with plates A and B having a 2.0 cm separation. Since complete collection of the electrons in the beam is of great importance to these measurements, careful design of the electron collector is essential. The present collector is made from a 17.5×1.3 cm copper strip, 0.0063 cm thick, wound in a spiral and mounted on a copper disc base, so as to present the edge of the spiral to the electron beam. The depth of the Faraday cup so formed is in excess of ten times the separation of the spiral and the entrance area of the cup is 95 % open. Electrons which enter the cup will be trapped and collected along with any secondary electrons which may be produced within the cup. With this design of cup it is found that saturation of the electron current can be achieved with a positive bias potential of 9 volts on the cup relative to the collision region. The ability to use such a small positive bias reduces the possibility of ions, produced outside the collision region, being pushed into the collision region and so contributing to the ion current, giving the ion current a falsely high value.

In order to help collimate the electron beam and to prevent scattered electrons reaching the ion collector plates, the whole chamber is immersed in an axial magnetic field of 400 G supplied by a solenoid surrounding the chamber.

At the time the electrons are undergoing collision in the target region this volume should be field free. For this reason the electron beam and ion collector voltages are pulsed. A $0.5 \mu\text{s}$ pulse of electrons is produced which is collected in the electron collector leaving the slower moving ions behind in the target volume. $0.5 \mu\text{s}$ later a $6 \mu\text{s}$ ion

pusher voltage pulse is applied to plates A, 6 and 7 so pushing all the ions to the ion collector plate B. A minimum positive voltage pulse of 70 V is found necessary to achieve complete collection of all ions. Ions formed outside the target volume are prevented from being collected by keeping this region at the highest potential in the chain during the ion collection period.

The experimental procedure for measuring the ionization cross section is to measure the ion current, $I_i(\epsilon)$, at a measured electron beam current, $I_e(\epsilon)$, at a known incident electron energy, ϵ . Equation (1) then becomes

$$I_i(\epsilon)/I_e(\epsilon) = 3.535 \times 10^{16} P(273/T) L Q_i(\epsilon) \quad (4)$$

where P is the measured pressure in Torr, and T is the absolute temperature of the target gas, L is in cm and $Q_i(\epsilon)$ is in $(\text{cm})^2$.

The electron collision path through the target region, L , is complicated since the trajectory of such an electron in an axial magnetic field is not necessarily a straight line because of the lens system of apertures and because of elastic scattering of the electrons out of the beam. These effects have been shown to be negligibly small by Asundi (1963) and by Rapp and Englander-Golden (1965). Applying the arguments used by Rapp and Englander-Golden (1965) to our apparatus, the maximum error in L due to these effects is calculated as 0.2%. Hence the geometric length of the collision chamber was taken for L . Since it is impractical to include the pressure gauge inside the collision volume, the gauge was mounted on the manifold, a procedure that would have presented no difficulties in a static system since the temperature was constant in these regions. However, in order to maintain as low a background gas impurity as possible, the gas was allowed to flow through the system. Hence the pressure measured was not the true pressure of the collision region but a constant multiple of it. The cross sections obtained from the graphs of $I_i(\epsilon)/I_e(\epsilon)$ against P were thus relative cross sections only. These were then normalized by a determination of Q_i at $\epsilon = 70$ eV in a static system.

Contact potentials within the chamber were reduced to a minimum by gold plating the whole of the inside of the chamber. Despite this precaution the actual electron energy was found to be 0.60 eV lower than the voltage difference between the cathode and the collector region when the low energy cross sections were extrapolated back to threshold. Threshold in this type of experiment is not the spectroscopic threshold but, as has been shown by Asundi and Kurepa (1965), is $2kT$ below the spectroscopic threshold where T is the cathode temperature. Accordingly, the energy scale has been adjusted to give $Q_i = 0$ at $\epsilon \leq 15.45$ eV.

2.2. The ionization coefficient chamber

The ionization chamber in which the ionization coefficient of an electron swarm is measured consists essentially of a circular, parallel plate electrode assembly. These electrodes, 10 cms in diameter, are gold plated so as to present a chemically inert surface to the discharge. The cathode is 2 cms in diameter and is surrounded by a 4 cm wide guard ring while the anode is 2.5 cm in diameter surrounded by a 3.75 cm wide guard ring. The anode is mounted on a micrometer bellows vacuum lead-through enabling the inter-electrode gap to be varied from 0 to 2.16 cm. This assembly is mounted inside a 25 cm diameter cylindrical vacuum vessel. Three side arms in the vacuum vessel allow for the chamber to be pumped, for ultraviolet light to be admitted at glancing incidence on the cathode to produce the initial photoelectric current, I_0 , and for the UV light reflected from the cathode to be monitored. Potential differences were applied

between the electrodes from a Fluke model 412B, 2.1 kV power supply with an accuracy of 0.5%, and currents were read to an accuracy of 2% from a Keithley model 610 electrometer. An NRC Alphatron gas pressure gauge mounted on the manifold was used to measure static gas pressures to within 0.5% after calibration, *in situ*, against the MKS Baratron secondary standard.

3. Results

3.1. Hydrogen

Measurements of the total ionization cross section in hydrogen have been made in the energy range threshold to 500 eV. These results are presented in table 1 where they are compared with the previous results of Rapp and Englander-Golden (1965), Tate and

Table 1. Total ionization cross sections in hydrogen. (Weight should not be attached to the final decimal place of the present results.)

Electron Energy (eV)	$Q_i \times 10^{16} \text{ (cm}^2\text{)}$			
	Present	Rapp and Golden (1965)	Tate and Smith (1932)	Harrison (1956)†
16	0.0300	0.0299	0.0051	0.053
17	0.0924	0.0922		
18	0.155	0.156		
19	0.211	0.220		
20	0.264	0.280		0.50
21	0.314	0.336	0.297	
22	0.362	0.389		
23	0.410	0.439		
24	0.460	0.484		
25	0.505	0.525		
30	0.695	0.688	0.668	
35	0.806			
40	0.866	0.865		1.17
45	0.907	0.911		
50	0.942	0.940		
60	0.978	0.966		1.34
70	0.979	0.972		
80	0.978	0.962		1.32
90	0.961	0.947		
100	0.941	0.923	0.950	1.28
125	0.886	0.863	0.889	
150	0.831	0.813	0.833	
175	0.780			
200	0.737	0.715	0.730	0.905
250	0.660	0.636	0.645	
300	0.598	0.573	0.574	
350	0.544	0.518	0.526	
400	0.501	0.476	0.467	0.60
450	0.455	0.439	0.424	
500	0.416	0.407	0.396	

† Harrison's results taken from figure 12 of L J Kieffer and Gordon H Dunn (1966).

Smith (1932) and Harrison (1956). It is immediately evident that the present data is not in agreement with the values presented by Harrison.

For $\epsilon \geq 30$ eV however, the present results lie within 4% of both the Tate and Smith and the Rapp and Englander-Golden values. Since $\pm 4\%$ is our estimated possible error in our absolute cross sections and Rapp and Englander-Golden claim a $\pm 4.5\%$ possible error, this constitutes agreement. Below 30 eV however our value of Q_i are up to 8% lower than those of Rapp and Englander-Golden. Of all the factors involved in the measurement of Q_i only two can give an error in this direction, incomplete collection of ions and an error in calibration of the pressure gauge. This latter error would be constant throughout the energy range and hence cannot explain the observed discrepancy. Also, the method of calibration of the pressure gauge described previously could lead to a maximum error of only $\pm 2\%$. Tests of the ion collection voltage pulse indicate that increasing neither the pulse height nor the pulse length increases the number of ions collected.

It is possible that incomplete collection of the electron current at low energy in previous work may have lead to falsely high values of Q_i . It is believed that the design of the present electron collector cup minimizes this effect.

A more likely explanation for the observed discrepancy is the presence in previous determinations of Q_i of the transverse ion collection field in the target volume while the ionizing collisions are occurring. This transverse field will inevitably have a larger effect on the slow electrons than on the fast electrons, tending to increase their path through the target volume and hence give high values of Q_i . The present method of pulsing both the electron beam and ion collector fields eliminates this possible error.

The first ionization coefficients in hydrogen obtained in the present work are shown in figure 2. These values were obtained by applying the Gosseries analysis (Haydon and Robertson 1961) to the current growth data at each value of E/N over the range $70 \text{ Td} \leq E/N \leq 750 \text{ Td}$, ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). The lower limit was set by the rapid increase in error as the electron amplification approaches zero while the upper limit was imposed by the onset of non-equilibrium effects. Analysis of current growth data for $E/N = 985 \text{ Td}$ indicates that α/N is no longer a function of E/N alone but is a function of position in the gap and of the gas number density. In these conditions α/N is observed to decrease by as much as a factor of six ($42.5 \times 10^{-17} \text{ cm}^2$ to $7.0 \times 10^{-17} \text{ cm}^2$) across the gap. It is interesting to note that if the high Nd sections only of the current growth curves at $E/N = 985 \text{ Td}$ are analysed a value of $\alpha/N = 7.1 \times 10^{-17} \text{ cm}^2$ is obtained in agreement with Haydon and Robertson (1961) and Fletcher and Haydon (1966) while analysis of the whole current growth curves gives an average $\alpha/N = 10.5 \times 10^{-17}$ as suggested by Chanin and Rork (1963). Within the swarm energy range considered in figure 2 no evidence of non-equilibrium was apparent. The present data substantially agrees with the results of Haydon and Stock (1966) and with Fletcher and Haydon (1966).

The fundamental relationship between Q_i and α/N given in equation (3) requires knowledge of the electron energy distribution function $F(\epsilon)$. In hydrogen this function has been calculated by Lucas (1969) and measured experimentally by Kenny and Craggs (1970). The present values of Q_i have been used in equation (3) along with the values of $F(\epsilon)$ available to predict α/N . The predicted values of α/N , at $E/N = 170 \text{ Td}$ and $E/N = 280 \text{ Td}$, for each set of $F(\epsilon)$ considered is compared with the present experimental values of α/N in table 2. Diffusion effects have been taken into account (Burch and Huxley 1967). At both values of E/N good agreement between theory and experiment is observed when Lucas' $F(\epsilon)$ data is used. At $E/N = 170 \text{ Td}$ and using the Kenny and Craggs $F(\epsilon)$ values, however, the predicted α/N is about one half of the experimental

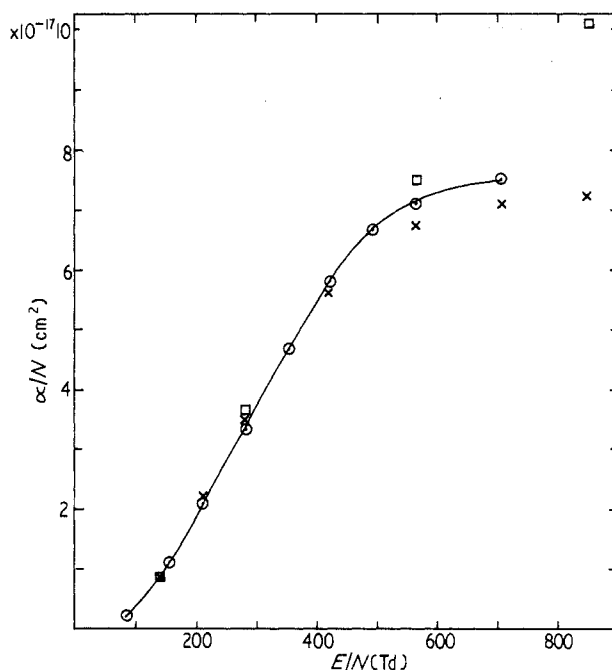


Figure 2. α/N as a function of E/N in hydrogen. —○— present results; □ Chanin and Rork (1963); × Haydon and Robertson (1961).

Table 2. Comparison of α/N calculated from the present values of Q_i using various forms of $F(\epsilon)$ with the present experimental values of α/N .

		$\alpha/N \times 10^{17} \text{ (cm}^2\text{)}$			
$E/N(\text{Td})$	$f(\epsilon)$	Kenny and Craggs (1969)	Lucas (1969) Curve A	Lucas (1969) Curve C	Present Experimental
170	0.66		1.43		1.37
280			3.32	3.43	3.39

value. As may be seen from table 2 it was not possible to decide which of the Lucas curves, designated A and C by him, gives the better agreement.

3.2. Deuterium

The present ionization cross sections for deuterium are given in column 1 of table 3. In column 2 of this table the results of Rapp and Englander-Golden (1965) are listed for comparison. The present results are in good agreement with those of Rapp and Englander-Golden except, as in the case of hydrogen, at $\epsilon \leq 25$ eV. At these low electron energies the discrepancy in deuterium is as much as 10% at $\epsilon = 22$ eV and, as with hydrogen, can be explained by the presence of a constant ion withdrawal field.

Comparison of the present results of Q_i presented in tables 1 and 3 show that the absolute ionization cross sections for the two gases are very similar in both the shape of

Table 3. Total ionization cross sections in deuterium. (Weight should not be attached to the final decimal place of the present results.)

Electron energy (eV)	$Q_i \times 10^{16} \text{ (cm}^2\text{)}$	
	Present	Rapp and Golden (1965)
16	0.034	0.034
17	0.097	0.104
18	0.159	0.173
19	0.218	0.239
20	0.273	0.300
21	0.325	0.355
22	0.378	0.404
23	0.423	0.454
24	0.470	0.498
25	0.515	0.537
30	0.700	0.699
35	0.809	—
40	0.876	0.876
45	0.917	—
50	0.951	0.950
60	0.977	0.977
70	0.986	0.981
80	0.981	0.974
90	0.964	0.958
100	0.946	0.939
125	0.890	0.877
150	0.833	0.813
175	0.781	—
200	0.735	0.716
250	0.661	0.638
300	0.604	0.576
350	0.553	0.523
400	0.510	0.482
450	0.469	0.446
500	0.431	0.414

the Q_i against ϵ curves and in absolute magnitudes, the maximum of the deuterium curve being less than 1 % above the hydrogen maximum.

Figure 3 shows the ionization coefficients in deuterium as a function of E/N . The only previous results with which we can compare our data are those of Rose (1956) and Davies *et al* (1961). For $E/N < 300$ Td the present data agree well with those of Rose whereas at higher E/N excellent agreement is observed with the results of Davies *et al*. This trend we believe to support the contention that Rose's results are incorrect at high E/N because he did not correct his current growth data for secondary effects in evaluating α/N .

It is not possible to compare our experimental ionization coefficients with the values of the ionization coefficients predicted by our ionization cross sections inserted into equation (3) since no published electron swarm distribution functions exist for deuterium. Such a function could be expected to be similar to that for hydrogen, at any given E/N , at higher electron energies ($\epsilon > 5$ eV) since the excitation and ionization cross sections

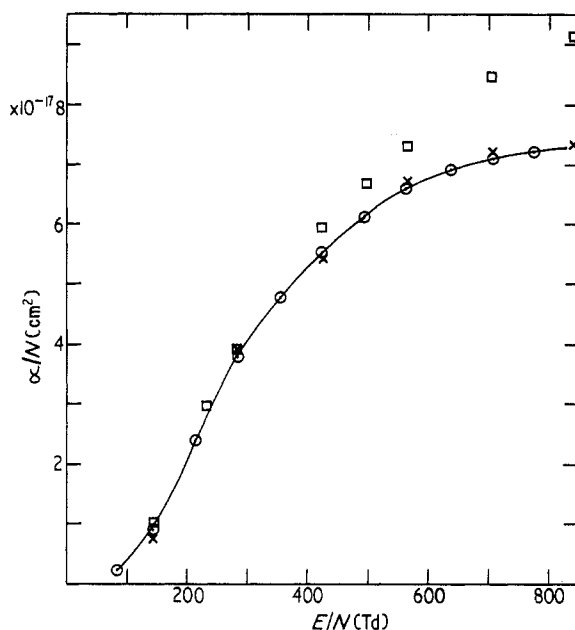


Figure 3. α/N as a function of E/N in deuterium. —○— present results; \times Davies *et al* (1961); \square Rose (1956).

are very similar. At low ϵ however the momentum transfer cross section may be different due to the larger mass of the deuterium molecule so resulting in a different electron energy distribution for $\epsilon < 5$ eV. Since it is the distribution function at low ϵ that determines the electron drift velocity, W , and since α/N is in turn dependent upon W^{-1} , the parameters of the low energy electrons in the swarm are of great importance to the magnitude of α/N . $F(\epsilon)$ could be calculated if W were known over the range of E/N considered here (Fletcher and Burch 1972). Unfortunately no such data appear to exist.

4. Conclusion

We have measured the total absolute electron impact ionization cross sections to within $\pm 4\%$ over the energy range threshold $< \epsilon < 500$ eV and the electron swarm ionization coefficient from $85 \text{ Td} < E/N < 700 \text{ Td}$ in both hydrogen and deuterium. The present relative ionization cross sections are estimated to be accurate to within $\pm 1\%$.

In both hydrogen and deuterium good agreement is observed for Q_i between the present results and those of Rapp and Englander-Golden (1965) except at energies near to threshold. While it is very difficult to explain such discrepancies, it is believed that the difference is due to not having the transverse ion withdrawal field present when the electron-molecule collisions occur in our pulsed method.

The values of α/N measured in the present work agree well with those of Haydon and Robertson (1961) and of Fletcher and Haydon (1966) for hydrogen and with those of Davies *et al* (1961) for deuterium. Also the present values of Q_i and α/N in hydrogen along with the theoretical values of Lucas (1969) for the energy distribution function of the electron swarm, $F(\epsilon)$ are found to constitute an internally consistent set of data.

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