

Measurement of Barium Vapor Density

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**I N S T I T U T F Ü R P L A S M A P H Y S I K**

**G A R C H I N G B E I M Ü N C H E N**

# INSTITUT FÜR PLASMAPHYSIK

GARCHING BEI MÜNCHEN

## Measurement of Barium Vapor Density

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Abstract

The density of atomic barium emitted from a small aperture in a uniformly heated stainless-steel oven has been measured by the method of resonance fluorescence. The range of the oven temperature was  $730^{\circ} - 1200^{\circ}\text{K}$ . At lower densities, the resonance transition  $6s^2\ ^1S \leftrightarrow 6s\ p\ ^1P$  was used for the density measurements, at higher densities the forbidden transition  $6s^2\ ^1S \rightarrow 6p\ s\ d\ ^3P$  or  $^3D$ , followed by emission through the allowed transitions to  $6s\ 5d\ ^3D$ . From the measured spatial distribution of the density above the aperture, the equilibrium vapor density in the oven was deduced. The latter can be expressed empirically reasonably well by the formula

$$N_0(T) = 1.6 \times 10^{22} \exp[-19000/T] \text{ cm}^{-3}$$

with the temperature  $T$  in  $^{\circ}\text{K}$ . At temperatures higher than  $1000^{\circ}\text{K}$  the measured densities were progressively slightly lower than this formula predicts. However, the deviation could be due to certain systematic errors in the measurement which became progressively more serious with increasing density. In addition to the barium density, the measurements yielded some information on the atomic transitions employed, generally confirming previous knowledge in this matter.

## I. Introduction

The knowledge of the equilibrium vapor pressure of barium appears to be in a relatively unsatisfactory state. The International Critical Tables [1], for example, lists three entries, two of which, measurements by Rudberg and Lempert [2] and by van Liempt [3] are in good agreement with each other, but the third [4] evidently considered the most reliable, gives vapor pressures almost exactly a factor 10 larger. Nesmeyanov [5] after detailed criticism concludes that no presently available data on vapor pressure of solid barium is reliable. (Ref. [4] is not mentioned by Nesmeyanov, presumably because of its restricted availability.)

In recent years, barium is becoming increasingly popular in low-temperature plasma research [6 - 11] because of its multiple virtues in the field of plasma diagnostics. It is therefore particularly important that the vapor pressure of neutral barium should be determined and predictable, since otherwise a number of uncertainties in the creation and subsequent behavior of the plasma is inevitable.

In the present paper we describe the results of measurements of atomic barium density emitted from an oven that was designed as a barium source for a Q-device [7, 8]. From these measurements the density in the oven, and hence the vapor pressure, can be deduced. The measurement is thus effectively by the Knudsen effusion method, except that the vapor density is determined by the (for this purpose) novel method of resonance fluorescence.

## II. Description of the Measurements

The experimental arrangement for the vapor density measurement is shown schematically in fig. 1. The barium oven, shown in the inset in more detail, is located on the z-axis. The size of the barium beam in the measurement position may be regulated by means of a cooled aperture limiter. A high-pressure Xe arc lamp, located under these conditions, the barium density above the aperture should be determined only by the solid angle subtended by the

in the y-direction, is focussed onto the measurement position, and the fluorescent radiation is detected by means of a monochromator in the x-direction. The observing beam (i.e. the field of view of the monochromator) may be moved along the y-direction by means of a variable angle prism. Scans of length of the order of 1/10 or less of the illuminating focal distance may be made without correcting the latter. Similarly, a scan in the x-direction could be made by moving the illuminating beam, although for the present experiments this was superfluous because of the good cylindrical symmetry of the barium beam.

The stainless steel barium oven has an essentially cylindrical shape, with internal radius 22 mm, and height 25 mm. It can be heated up to about 1200 °K by means of a bifilar thermo-coax-wire, wound around the circumference and the top of the cylinder. The inside temperature is measured by means of a Ni-Cr Ni thermocouple, which extends about 8 mm inside the oven, as shown in the diagram. On the outside of the oven, there is a copper gauge in good thermal contact with the stainless steel walls, assuring a uniform temperature of the oven, while allowing direct observation of the stainless steel surface. In addition to the thermocouple, the temperature, and particularly the temperature distribution, was determined by visual comparison of the oven brightness with a calibrated tungsten ribbon lamp, and also with an optical micropyrometer. The variation of the temperature of the oven walls was less than about 10° over the entire surface, with the exception of the end of the thermocouple pipe, which extended some 4 mm below the copper shield, and had typically 20 - 25° lower temperature than the body of the oven.

The oven aperture has a diameter of 2.2 mm, i.e. an area of about 1 per cent of the inside cross section of the oven which should represent the minimum evaporating area. Thus the disturbance of the vapor equilibrium by the effusion should be negligible. The thickness of the walls of the aperture is about 1 mm, with a shape as shown in fig. 1, inset.

Under these conditions, the barium density above the aperture should be determined only by the solid angle subtended by the

aperture at the point in question, and the equilibrium density in the oven,  $N_0(T)$ . In particular, on the z-axis, and for  $z \gg a$ , the radius of the aperture, the density should be

$$N(0, z) = \frac{a^2}{4z^2} N_0(T) \quad (1)$$

and at a point  $(y, z)$  the density should be

$$N(y, z) = \left(1 + \frac{y^2}{z^2}\right)^{-3/2} N(0, z) = \cos^3 \theta N(0, z) \quad (2)$$

where  $\theta$  is the polar angle. These relationships were checked directly, by moving the oven in the z-direction, and scanning with the variable prism in the y-direction.

The Xe arc used for the illumination has a maximum brightness corresponding to a black body of roughly 5400 °K (at the wavelengths of present interest), and dimensions of the order of 1 mm, i.e. small compared to any dimensions of interest in the barium beam. Its spatial brightness distribution is rather complicated. However, by suitable averaging we can, for the purposes of discussion, replace the actual lamp by a rectangle of width  $W$ , and an effective brightness

$$i(\lambda) = \frac{1}{W\Delta z} \iint i(x, z) dx dz \quad \text{photons/cm}^2\text{-sec-sr-unit } \Delta\lambda \quad (3)$$

at the resonance wavelength  $\lambda$ . Here  $i(x, z)$  is the actual brightness of the lamp at  $(x, z)$ , and  $\Delta z$ , the effective height of the arc, is given by projecting the image of the monochromator slit length (which is of course oriented in the z-direction) back to the arc lamp by the illuminating optics.

The brightness of the fluorescent radiation measured by the monochromator is then given by

$$I(\lambda^*) = pq \tau \frac{\Omega}{4\pi} i(\lambda) \frac{\pi e^2 \lambda^2}{m c^2} f N_{Ba} MW \quad \text{photons/cm}^2\text{-sec-sr} \quad (4)$$

Here  $M$  is the magnification of the illuminating optics, so that  $MW$  is the geometrical depth of the illuminated region (in the x-

direction);  $\Omega$  and  $t$  are the solid angle subtended at the measuring point by the exit pupil of the illuminating optics, and the transmittance of the optics, respectively;  $f$  is the oscillator strength for the resonance excitation;  $q$  is the branching ratio for the observed radiation at  $\lambda'$ , i.e. the probability of emission of radiation in the line  $\lambda'$  multiplied by the radiative lifetime of the upper state;  $p$  is an isotropy factor arising from the polarization of the emitted radiation [12].

The relevant transitions [13] in Ba I, together with the wavelengths (in Angstroms) and the absorption oscillator strength [14] are shown in fig. 2a. The forbidden transitions between the configuration  $6s^2$  and  $6p\ 5d$  are shown in dashed lines. In addition, certain other energy levels and transitions are indicated by dotted lines for easier orientation, although these were not used in the present work.

In the case of the singlet resonance lines,  $\lambda\ 5535$ , the observed line is the same as the exciting line ( $\lambda' = \lambda$  in eq.(4)) and  $q = 1$ , since the transition to  $6s\ 5d^1D$  is of negligible strength. The line emitted in the  $x$ -direction should be linearly polarized in the  $z$ -direction, and the unisotropy factor  $p = 3/4$  (i.e. the re-emission in  $y$ -direction should be twice as strong as that in the  $x$ - and  $z$ -direction. Customarily the "preferred" direction in the absorption or emission processes is designated as the  $z$ -axis. We hope that no confusion arises from our designation of the incident light, which in the present case determines the anisotropy, as the  $y$ -axis). The polarization in this, as well as the other cases mentioned below, were also experimentally observed.

In the other three cases, the observed lines are the strongest allowed transitions from the upper levels:  $\lambda\ 3889$  excitation observed through  $\lambda'$  6063-5997 (with  $q = 0.69$  and  $0.31$  respectively);  $\lambda\ 4134$  through  $\lambda'$  6595-6675 (with  $q = 0.67$  and  $q = 0.33$ , respectively), and  $\lambda\ 3501$  through  $\lambda' = 5826$  (with  $q = 0.78$ ). The last-mentioned transition has an excitation probability of only 10 times weaker than the resonance line,  $\lambda\ 5535$ , and it requires

quartz or special glass optics for the excitation. Thus, although we could observe it with apparently correct intensity according to ref. [14], it did not contribute significantly to the density determination and will not be mentioned further. Of the two triplet transitions, the lines  $\lambda' 6063$  and  $\lambda' 6675$  arise from  $J = 1 \rightarrow J = 2$  transitions in which  $\Delta M = 0 \pm 1$  (with respect of the incident light direction) all occur with equal probability. These lines are therefore unpolarized and isotropic, with  $p = 1$ . The other two lines,  $\lambda' 5997$  and  $\lambda' 6595$  arise from  $J = 1 \rightarrow J = 1$ ,  $\Delta M = 0$  is twice as probable as  $\Delta M = \pm 1$ . These lines are therefore preferentially polarized in the y-direction (as observed in the x-direction y-polarization twice as strong as z-polarization), and the unisotropy factor is  $p = 9/8$ . The other lines in the  $6s 5d - 6p 5d$  triplets, indicated by dotted lines in fig. 2b, should not be excited by absorption from the ground state because of the J-selection rule, and indeed were not observable in our experiments.

The reason for utilizing the forbidden transitions is avoidance of multiple scattering. In setting up eq.(4) it was assumed that the vapor is optically thin. This imposes the condition

$$\overline{Nl} \lesssim 2 \times 10^6 (\overline{\Delta V} + 10^3)/f \text{ cm}^{-2}$$

on the "line density"  $\overline{Nl}$ , where  $l$  is the path-length of the light beam in the vapor, and  $\Delta V$  (cm/sec) is some average velocity spread of the atoms along the line-of-sight (if the velocities were isotropic,  $\overline{\Delta V} \approx \overline{V}$ , the mean thermal velocity). Since  $\overline{\Delta V}$  is of the order of  $10^4$  cm/sec and  $l$  typically several centimeters, the singlet resonance line cannot be used for densities larger than about  $3 \times 10^9 \text{ cm}^{-3}$ . The use of the forbidden transitions allows an extension of this limit by more than two orders of magnitude. On the other hand, at low densities, i.e. at low temperatures or large distances from the oven, the singlet resonance line is indispensable, because of difficulties of detection aggravated by the reduced sensitivity of photomultipliers at the longer wavelengths.



### III. Experimental Results

In the measurement of the oven temperature, the thermocouple yielded consistently somewhat lower values than those determined from the oven surface brightness. The discrepancy was about  $30^{\circ}\text{C}$  at the higher temperatures, and increased gradually to nearly  $50^{\circ}\text{C}$  at the lower temperatures. The increase in the discrepancy may possibly be due to the increasing difficulty of the brightness determination at the lower temperatures. Perhaps  $10 - 15^{\circ}$  of the discrepancy may be due to the emissivity of the stainless steel which in the quoted measurements was assumed to be equal to that of tungsten. At the lower end of the temperature range, below about  $950^{\circ}\text{K}$ , where difficulties with multiple scattering were not serious, this temperature discrepancy constitutes the largest source of uncertainty in the measurements.

A sample of the measured spatial distribution of the barium vapor density above the oven is shown in fig. 3, at an oven temperature of  $780^{\circ}\text{K}$  (thermocouple). The measured density profiles, for four different distances  $z$  from the oven, are multiplied by  $z^2$  for convenience of representation. The constant height of the center of the different profiles demonstrates the  $z$ -dependence of eq.(1). The  $y$ -dependence at each  $z$  does not differ measureably from eq.(2). The  $z^{-2}$  dependence could be followed to considerably larger distances (up to 30 cm, utilizing data at different temperatures), but the profiles became too flat at higher  $z$  to test significantly the  $y$ -dependence at much larger  $z$ , because of the limited scanning range available. At much higher temperatures the spatial distribution near the oven aperture could not be determined, because the observation windows became coated with barium too rapidly. However, there seems no reason to expect any qualitative differences since even at the highest temperatures used the mean free paths of the atoms in the oven were still at least comparable to the oven dimensions, and much larger than the oven aperture.

With higher oven temperatures, a diaphragm was used to limit the size of the beam (fig. 1), and to protect the windows from the barium flux. Nevertheless, at the highest temperatures used

( $T \gtrsim 1100$  °K) various difficulties arose. As expected, the vapor became optically thick for the resonance line, as evidenced by changes in the shape of the observed density profile, and appearance of the polarization component parallel to the incident light beam. In some cases of moderate "saturation" or multiple scattering the effect could be approximately evaluated, and are shown with the data below. Secondly, in prolonged runs at high temperature, the oven aperture, and sometimes also the aperture diaphragm (e.g. 4 mm diameter, 10 mm from the aperture) became clogged with barium. This latter effect appears to be very unstable, i.e. once started it will very rapidly close the aperture completely. However, even in the best measurements at high temperatures it is possible that the aperture was already slightly reduced, and therefore the deduced vapor pressure too low. On the other hand, below  $\sim 1100^\circ$  the oven could apparently run indefinitely, at least for many hours, without noticeable effect on the aperture.

From the measured vapor density and the known geometry of the setup, the equilibrium vapor densities,  $N_o(T)$  are obtained from eq.(1), and the corresponding vapor pressures from the ideal gas law. The vapor pressures thus determined are shown in fig. 4. In all cases, the right-hand end of the data lines corresponds to the thermocouple measurement of temperature, and the left-hand end to the temperature deduced from the oven brightness. The measurements made with the resonance line are indicated by solid lines, those measured by means of the forbidden transition, by dotted lines. The three shaded areas at higher temperatures show estimated corrections for multiple scattering effects for the resonance line. The straight line drawn to the data "points" has the equation

$$\log_{10} p(\text{torr}) = 6.80 - \frac{8800}{T} \text{ } ^\circ\text{K} \quad (5)$$

Evidently, this is also the line that one would draw to the data of Rudberg and Lempert [2], also shown in fig. 4. We therefore conclude that, aside from slight uncertainties in the temperature, the results of ref.[2] and [3] are essentially correct, and hence

ref.[4] by about a factor 10 too high.

In most experiments, it is the density rather than the pressure that is of interest. From a graph of  $\log N$  vs.  $T^{-1}$  an equation comparable to eq.(5) is obtained, in exponential form,

$$N(T) = 1.6 \times 10^{22} \exp[-19000/T^{\circ}K] \text{ cm}^{-3} \quad (6)$$

with an accuracy of somewhat better than a factor two in the first constant, and not worse than  $\pm 1000$   $^{\circ}K$  in the second constant. If we were to identify the first constant with the density of solid barium, and the second with the heat of sublimation, the latter would be  $1.65 \pm 0.1$  eV, in the neighborhood of  $T = 900$   $^{\circ}K$ .

For the relative line strengths of the  $\lambda 6063 - \lambda 5997$  lines we find the ratio to be  $2.3 \pm 0.1$ , in agreement with Penkin's 2.0. However, the intensity of the  $\lambda 6675$  line in our measurements was never sufficiently large to allow reliable measurements, so we cannot regard the discrepancy to be significant.

Comparison of densities determined by means of  $\lambda 5535$ ,  $\lambda 6063$ , and  $\lambda 6595$  lines shows an essential agreement within a scatter of results obtained with the same line of different days (i.e. a factor about 1.3 - 1.5). There may be a systematic tendency of the densities measured with  $\lambda 6063$  line to be slightly (30 - 40 %) too low, indicating possibly a too large value for the  $\lambda 3889$  oscillator strength (0.0088). However, the experimental uncertainties are too large to allow a definite statement on this point. Within the experimental errors our results must be regarded as a confirmation of Penkin's [14] information on the transition probabilities.

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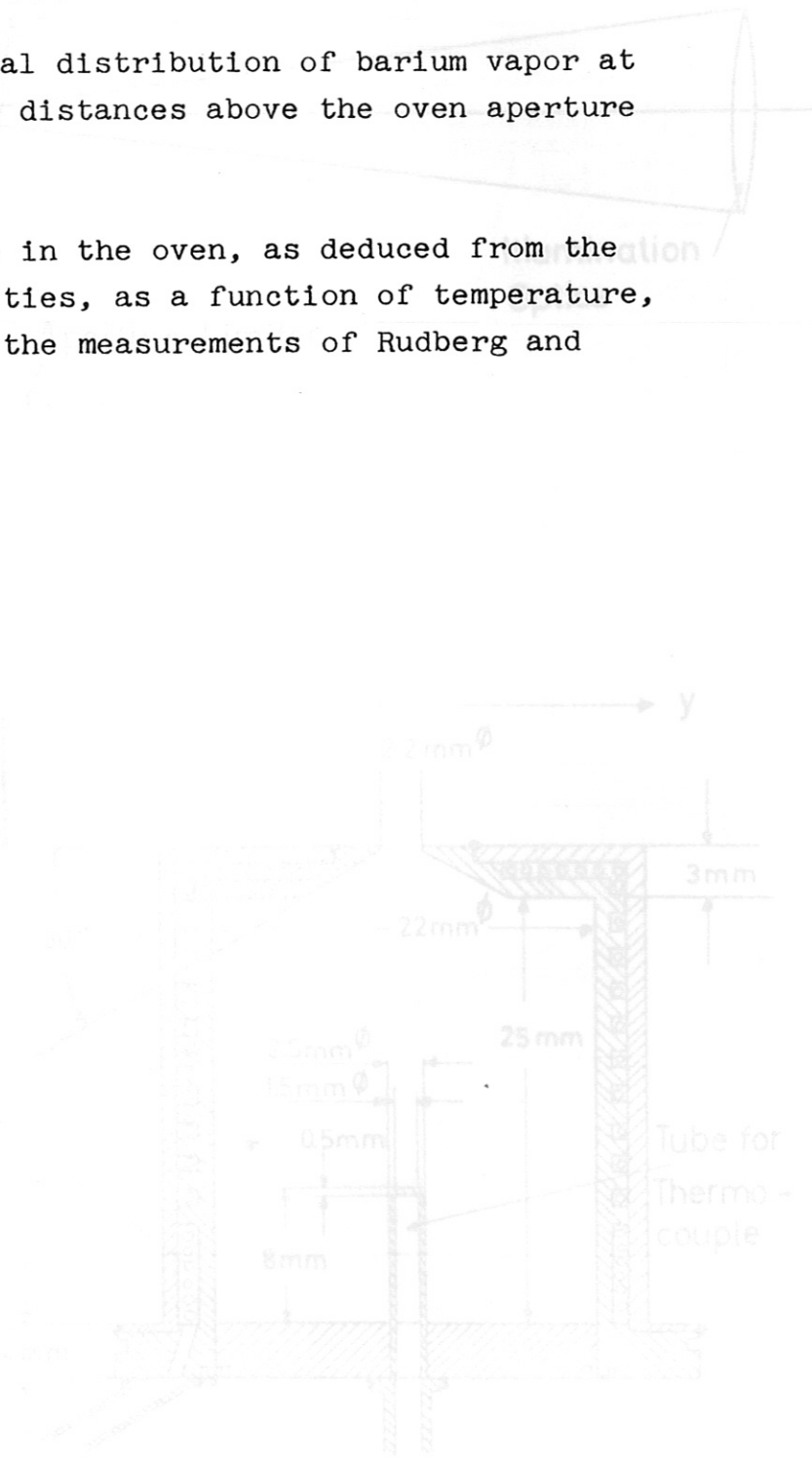
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Figure Captions

- Fig. 1 Experimental setup, and details of the barium oven
- Fig. 2 Partial energy level diagram of Ba I, showing the relevant transitions, wavelengths, and expected relative line strengths of the red triplets
- Fig. 3 Measured spatial distribution of barium vapor at four different distances above the oven aperture ( $Nz^2$  vs.  $y$ )
- Fig. 4 Vapor pressure in the oven, as deduced from the measured densities, as a function of temperature, compared with the measurements of Rudberg and Lempert [2]



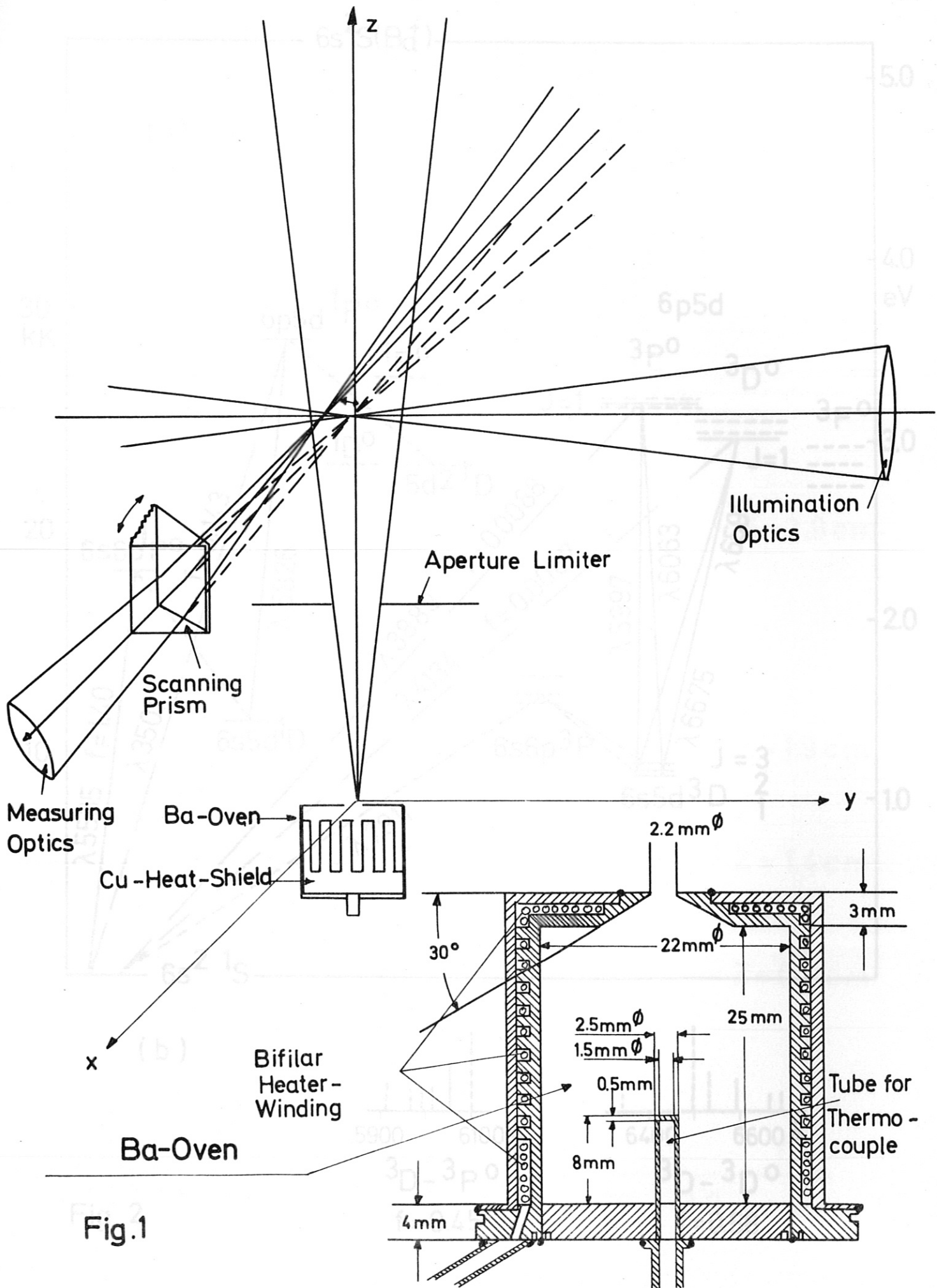
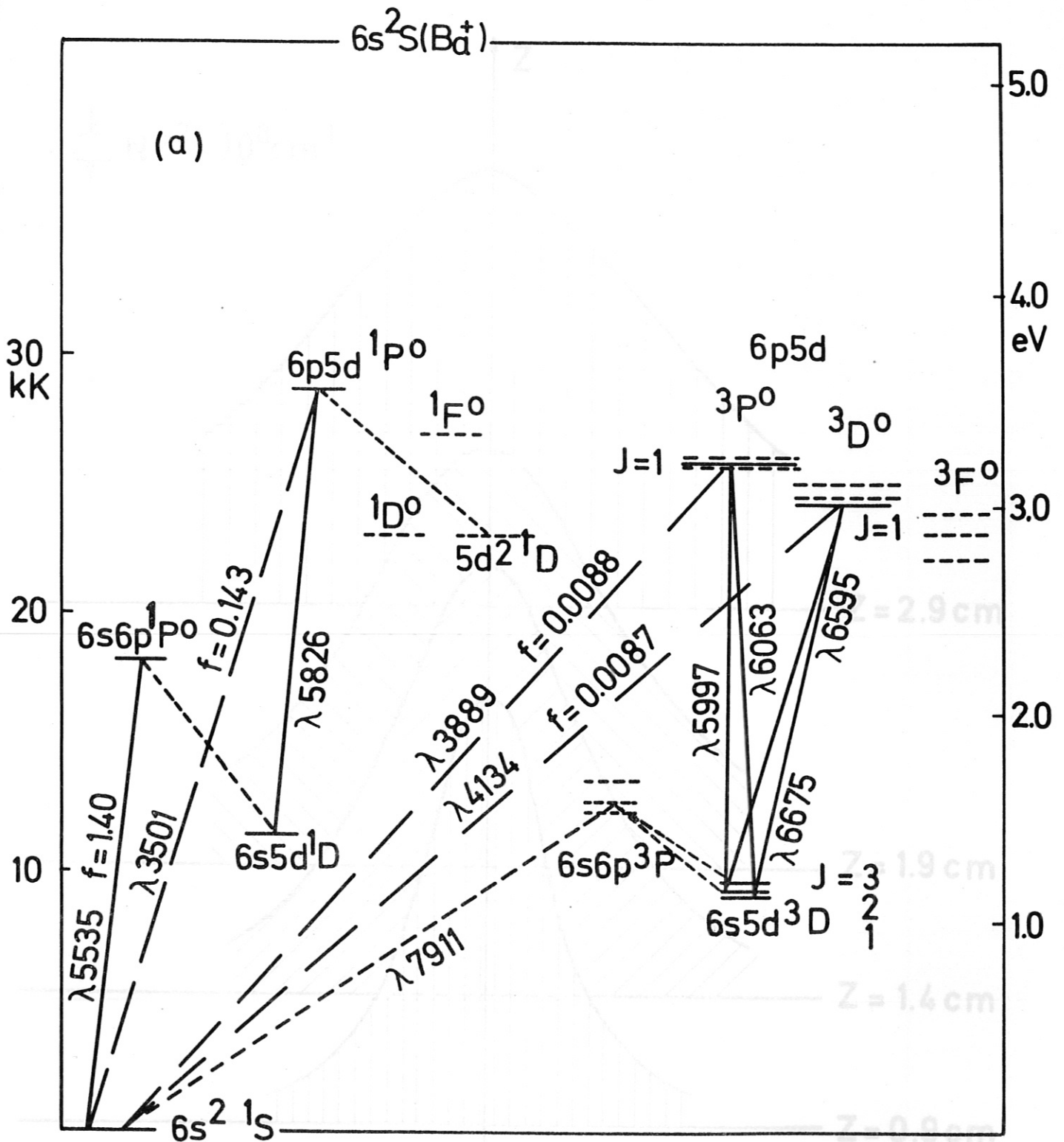


Fig.1





(b)

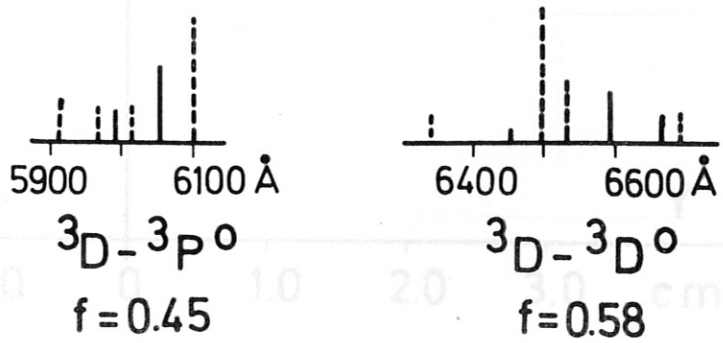


Fig. 2

Fig. 3

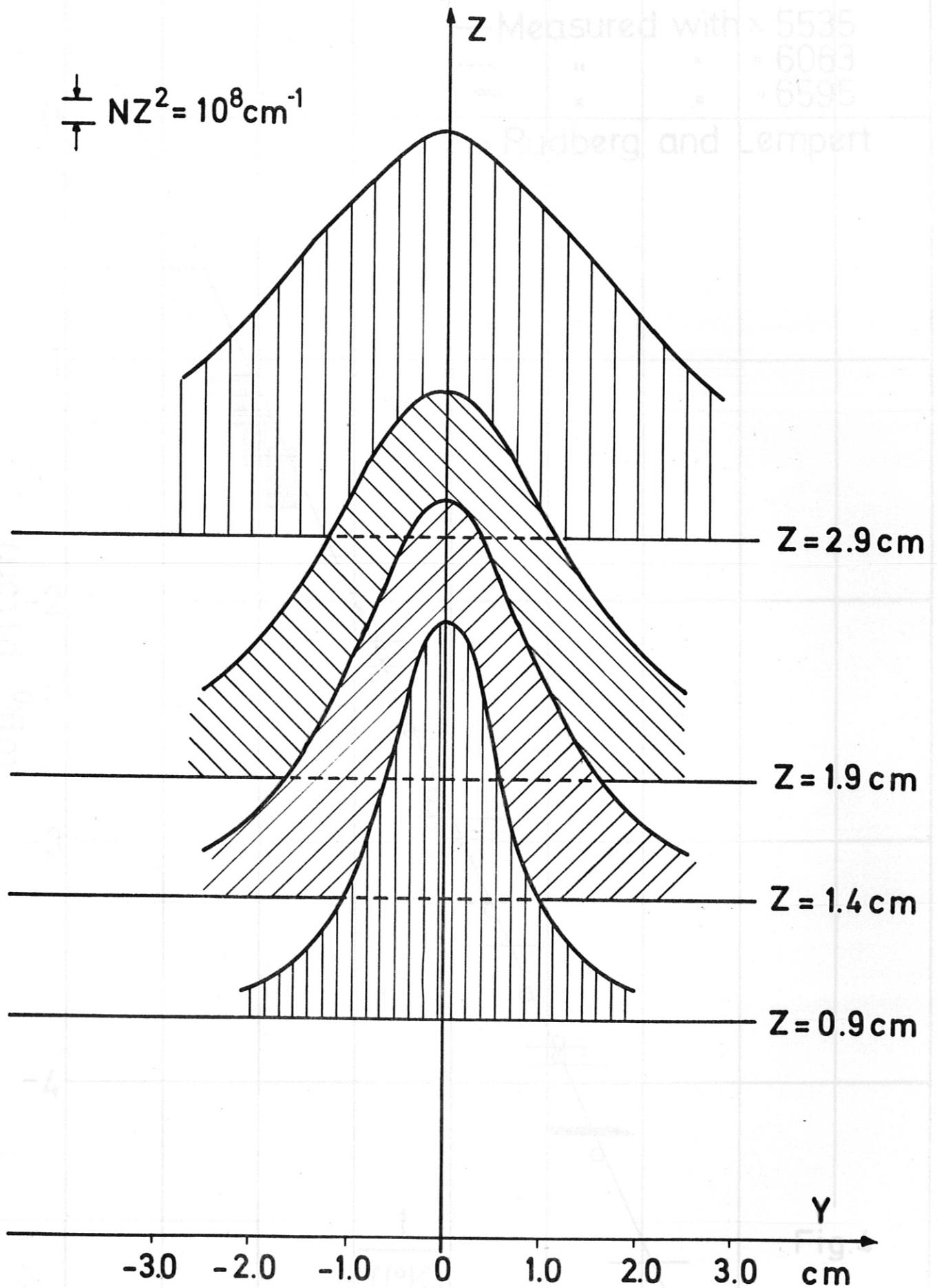


Fig. 3

$15 \times 10^{-4}$

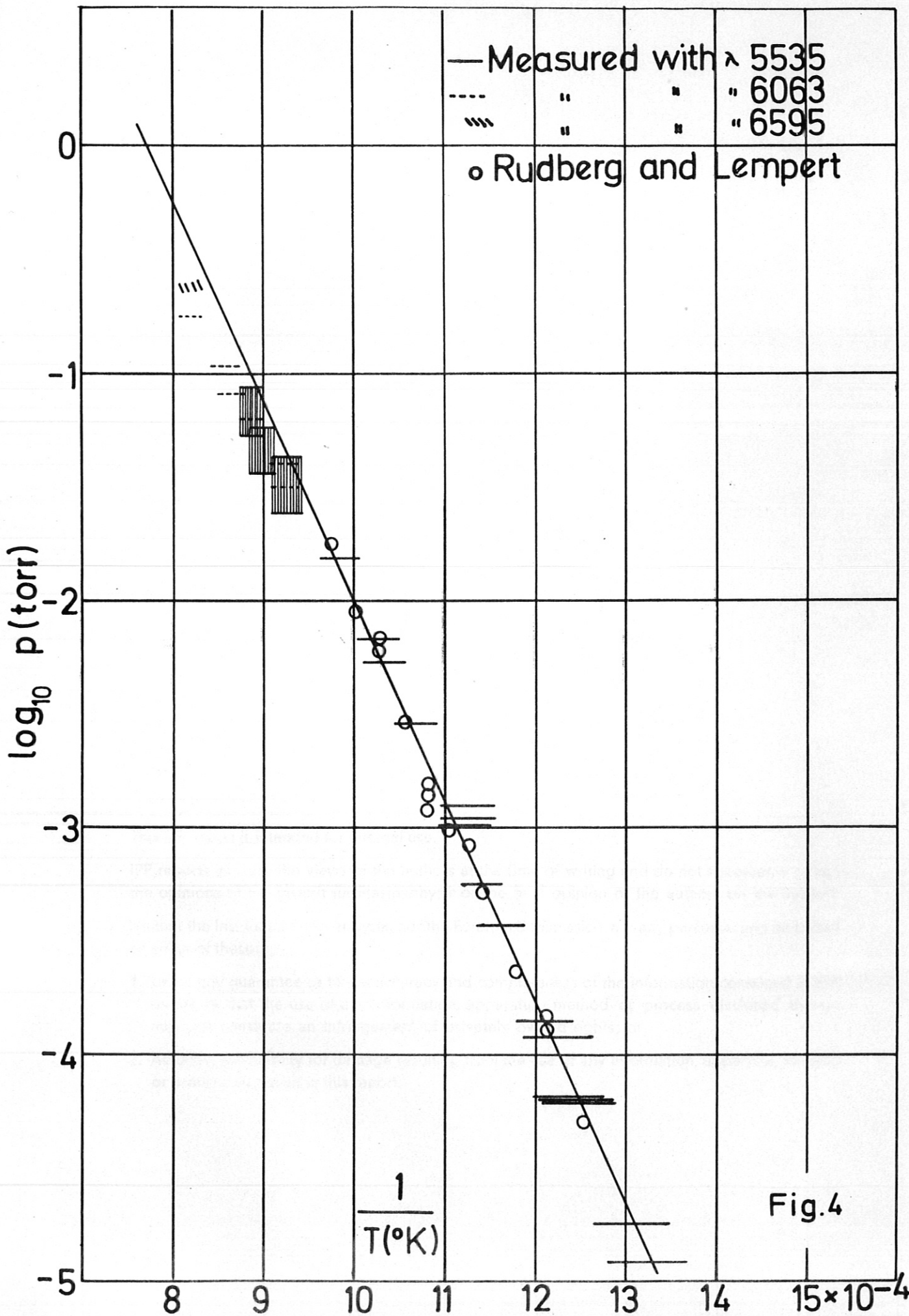


Fig.4