Chapter 4

Sinter Measurements

When liquid helium is cooled down by transmitting heat through a metal to the refrigerant, then the thermal contact between the liquid and the metal is crucial. The contact resistance can be improved by increasing the surface area with sintered powder. However, it should be also guaranteed that the sinter itself can be cooled. That means that both the surface area and the thermal conductivity through the sinter have to be optimised.

4.1 Sample Preparation

The silver powder was sintered onto a silver plated copper disc. Since the thermal conductivity of silver sinter is worse than that of the copper disc, the useful thickness of the sinter is only 1 or 2 mm. The copper disc was not annealed in order to avoid it becoming too soft.

Before plating, the disc was first cleaned in ethanol and acetone baths, and then etched in 40 % nitric acid HNO_3. The surface of the disc was scratched with a knife in order to make it easier for the sinter to bond. The electroplating was carried out in a mixture of acids when 0.08 A current (about 30 V voltage) was applied between the copper disc (cathode) and a silver bar (anode) for about 20 minutes. The current corresponds to 0.83 µmol/s flow of Ag^+ ions, thus the total volume of the silver plating, grown in 20 minutes, is about 10 mm^3. Since the total surface area of the disc with holder is about 40 cm^2, the thickness of the plating is about 2.5 µm, which should be enough for silver powder to be stuck on.

Both sides of the silver plated disc were sintered with 2×5 g of presintered powder (or powder which was first sintered in a similar manner described below and then crushed into groats). The presintered powder was pressed at room temperature with about 9 kN force (or 230 bar pressure) against the disc. Then the sample was heat treated at 200 °C for 20 minutes in open air. The resulting filling factor (or the density of the sinter compared to the density of the bulk silver) was about 46 %. The grain size of the used powder is about 0.2 µm [37].

4.2 BET Method for Surface Area Measurements

The surface area of the sintered silver powder can be determined with the BET (Brunauer, Emmett, Teller, 1938 [38]) method which is based on gas adsorption.

Let us assume that a gas molecule may adsorb to the clean metal surface or to the previous molecule layer releasing heat $E_{\mathrm{i}\to\mathrm{i}+1}$ when the number of molecule layers is increased from i by one. Suppose that the number of sites (in moles) for molecules on the metal surface, or the amount of gas required to form a monolayer, is n_{site}, and the total amount of adsorbed gas is n_{ads}. Furthemore let us define $n_{\mathrm{site},i}$ to be the number of sites (in moles) which has i layers of gas molecules adsorbed on top of each other. Thus

$$n_{\mathrm{site}} = \sum_{i=0}^{\infty} n_{\mathrm{site},i} \ , \quad n_{\mathrm{ads}} = \sum_{i=0}^{\infty} i n_{\mathrm{site},i} \ . \tag{4.1}$$

The number of sites which has i or less than i layers, $\sum_{j=0}^{i} n_{\mathrm{site},j}$, increases when a particle is evaporated from a site with $i+1$ particles, and the rate of this evaporation is proportional to $n_{\mathrm{site},i+1}$ and $\exp[-E_{\mathrm{i}\to\mathrm{i}+1}(k_{\mathrm{B}}T)]$ with proportionality factor $b_{i+1\to i}$. On the other hand, $\sum_{j=0}^{i} n_{\mathrm{site},j}$ decreases when a particle is adsorbed to a site with i particles, and the rate with what this happens is proportional to $n_{\mathrm{site},i}$ and the pressure p (or the collision rate) with proportionality factor $a_{i\to i+1}$. However, in thermal equilibrium $n_{\mathrm{site},i}$ are constant leading to

$$0 = \sum_{j=0}^{i} \dot{n}_{\mathrm{site},j} = b_{i+1\to i} n_{\mathrm{site},i+1} \exp\left(-\frac{E_{\mathrm{i}\to\mathrm{i}+1}}{k_{\mathrm{B}}T}\right) - a_{i\to i+1} n_{\mathrm{site},i} p \ . \tag{4.2}$$

It is reasonable to suggest that $E_{\mathrm{i}\to\mathrm{i}+1} = E'_{\mathrm{ads}}$, $a_{i\to i+1} = a'_{\mathrm{ads}}$ and $b_{i+1\to i} = b'_{\mathrm{evap}}$ are independent of the number of previously adsorbed gas layers when $i \geq 1$. However, parameters related to the clean metal surface are different and they are denoted by $E_{0\to 1} = E_{\mathrm{ads}}$, $a_{0\to 1} = a_{\mathrm{ads}}$ and $b_{1\to 0} = b_{\mathrm{evap}}$.

From Eqs. (4.1) and (4.2) it follows that the average number of layers is

$$\begin{aligned} i_{\mathrm{average}} &= \frac{n_{\mathrm{ads}}}{n_{\mathrm{site}}} = \frac{C_{\mathrm{BET}} x_{\mathrm{BET}}}{(1 - x_{\mathrm{BET}})(1 - x_{\mathrm{BET}} + C_{\mathrm{BET}} x_{\mathrm{BET}})} \ , \\ C_{\mathrm{BET}} &= \frac{a_{\mathrm{ads}} b'_{\mathrm{evap}}}{a'_{\mathrm{ads}} b_{\mathrm{evap}}} e^{\left(-\frac{E_{\mathrm{ads}} - E'_{\mathrm{ads}}}{k_{\mathrm{B}}T}\right)} \ , \\ x_{\mathrm{BET}} &= \frac{a'_{\mathrm{ads}}}{b'_{\mathrm{evap}}} p e^{\left(-\frac{E'_{\mathrm{ads}}}{k_{\mathrm{B}}T}\right)} \ . \end{aligned} \tag{4.3}$$

In the limit of the saturated vapour pressure p_0, the number of layers can grow to infinity, $i_{\mathrm{average}} \to \infty$, thus from Eq. (4.3) it follows that $x_{\mathrm{BET}} = p/p_0$ and Eq. (4.3) can be written as

$$\frac{p}{n_{\mathrm{ads}}(p_0 - p)} = \frac{1}{n_{\mathrm{site}} C_{\mathrm{BET}}} \left(1 + (C_{\mathrm{BET}} - 1)\frac{p}{p_0}\right) \ . \tag{4.4}$$

This is known as BET equation. Direct measurements have shown that the formula is valid in the range from $0.05p/p_0$ to $0.35p/p_0$ [38].

4.3 Surface Area Measurement

The surface area of the 10 g sinter sample was measured with the BET technique by adsorption of N_2-gas at liquid nitrogen temperature $T_{\mathrm{LN2}} = 77.36\,\mathrm{K}$, thus p_0 in Eq. (4.4) equals to the room pressure $p_0 = 1.021$ bar. The experimental setup, shown in Fig. 4.1, consisted of the sinter sample volume in liquid nitrogen bath, separated from pressure gauge and tunable volume V_{pistol} by Valve2. The system was connected to a pump and nitrogen gas bottle via Valve1. The amount of adsorbed gas n_{ads} was measured as follows. First both valves were opened, the tunable volume was zero, $V_{\mathrm{pistol}} = 0$, the sinter sample was cooled down to T_{LN2} and a certain pressure p was applied to the system. Next Valve1 was closed, the sinter sample was warmed up to the room temperature $T_0 = 295.15\,\mathrm{K}$ and the pressure was kept constant by increasing V_{pistol}. It was assumed that all adsorbed gas was evaporated at room temperature thus n_{ads} can be determined from the increase in volume V_{pistol}. The measurements were carried out at constant pressure in order to avoid problems with pressure dependent volume of the pressure gauge.

In order to be able to distinguish the amount of gas adsorbed from the thermal expansion of the non-adsorbed gas, the free volume of the experimental setup was minimised. The free volume of the sinter cell V_{free} was measured at room temperature. First the sinter volume was pumped and Valve2 was closed. Then the tunable volume was set to be $V_{\mathrm{pistol}} = 5$ ml and the pressure of the tunable volume and the pressure gauge was increased to be $p = 1.0$ bar by releasing some gas from the N_2 bottle. Then Valve1 was closed and Valve2 was opened and the pressure was kept constant by decreasing the volume V_{pistol}. The measurement gave the volume 2.05 ml from which the volume of the tube above the LN_2 bath, 0.3 ml, was subtracted, and so $V_{\mathrm{free}} = 1.75$ ml. Thus the thermal expansion of V_{free} at constant pressure indicates $\Delta V_{\mathrm{thermal}} = V_{\mathrm{free}}\,(T_0/T_{\mathrm{LN2}} - 1) = 4.93\,\mathrm{ml}$ change in volume.

Finally the amount of the adsorbed gas was calculated using the ideal gas relation

$$n_{\mathrm{ads}} = \frac{p\,(V_{\mathrm{pistol}} - \Delta V_{\mathrm{thermal}})}{R_{\mathrm{gas}} T_0} \,. \tag{4.5}$$

In the measurements the pressure was between 0.06 bar and 0.3 bar, and the measured volume between 8 ml and 12 ml, which can be clearly distinguished from the volume change due to the thermal expansion $\Delta V_{\mathrm{thermal}} = 4.93$ ml. The Eq. (4.4) together with the data plotted in Fig. 4.1 gives the number of the lattice sites $n_{\mathrm{site}} = 0.0336$ mmol and the BET constant $C_{\mathrm{BET}} = 24.1$. The area of one N_2 molecule is reported to be $0.162\,\mathrm{nm}^2$ [10], thus the surface area of the 10 g sinter sample is $3.3\,\mathrm{m}^2$ with 24 % error, or about $0.3\,\mathrm{m}^2/\mathrm{g}$.

Similarly also the area of the presintered powder was determined (see Fig. 4.2a). The measured area $\left(0.3^{+0.3}_{-0.2}\right)\,\mathrm{m}^2/\mathrm{g}$ of the presintered powder equals the area of the sinter.

In order to certify the reliability of the experimental setup, the area of the untreated powder was determined (see Fig. 4.2b). The area was measured to be $2.8\,\mathrm{m}^2/\mathrm{g}$ with 20 % error which is consistent with area from $3\,\mathrm{m}^2/\mathrm{g}$ to $5\,\mathrm{m}^2/\mathrm{g}$ given by the manufacturer [37].

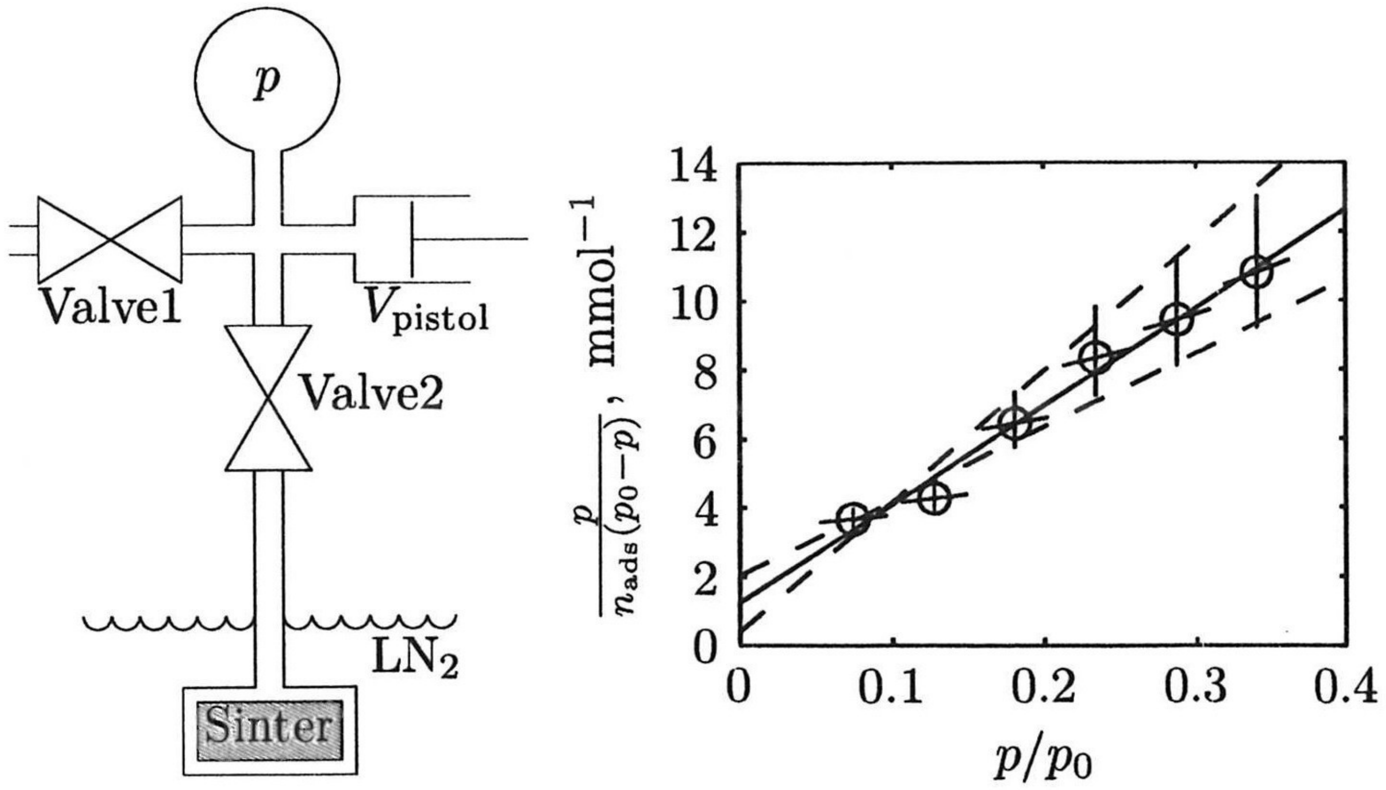

Figure 4.1: Experimental setup of the BET measurements and the measured data of the 10 g sinter sample plotted according to the BET equation, Eq. (4.4). The fitted solid line is $\frac{p}{n_{\mathrm{ads}}(p_0-p)} = 28.5\,\mathrm{mmol}^{-1} \cdot \frac{p}{p_0} + 1.23\,\mathrm{mmol}^{-1}$ which corresponds to $n_{\mathrm{site}} = 1/(28.5\,\mathrm{mmol}^{-1} + 1.23\,\mathrm{mmol}^{-1}) = 0.0336\,\mathrm{mmol}$. The vertical error bars represent the volumetric error and the almost horizontal bars are the errors due to the measured pressure.

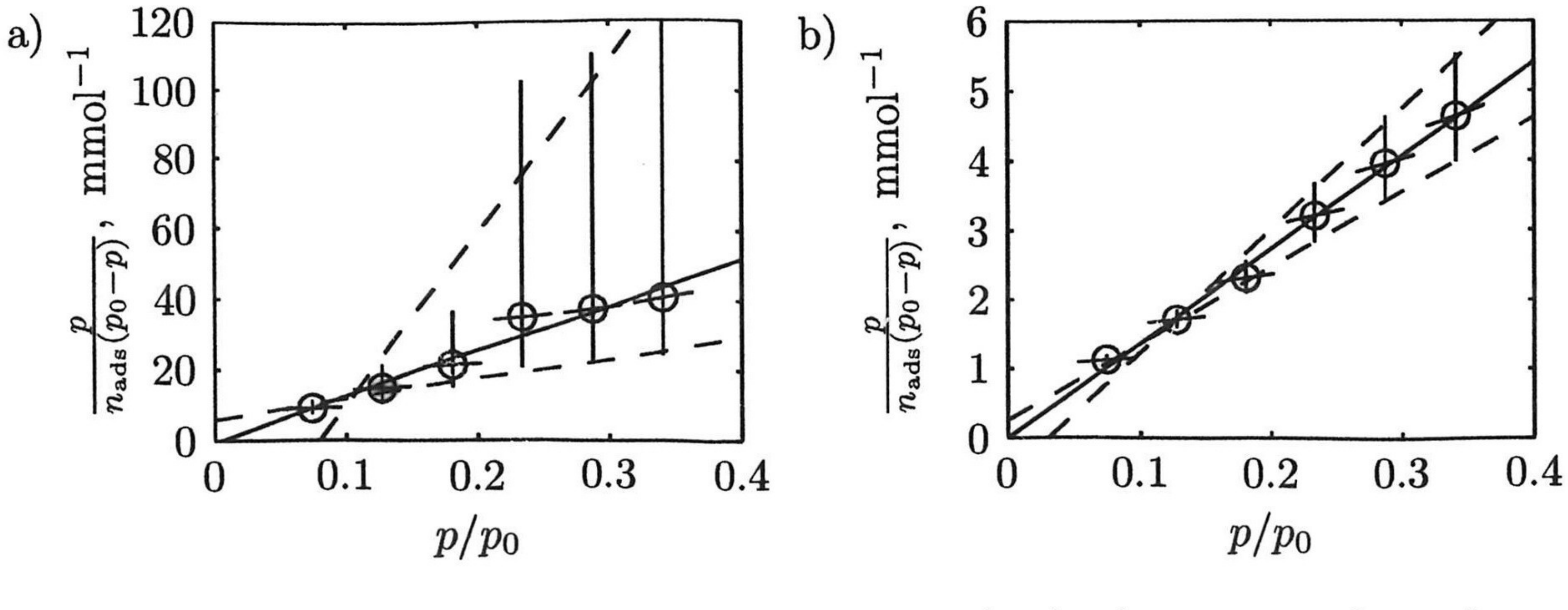

Figure 4.2: BET measurements according to Eq. (4.4): a) Presintered powder, 2.6 g: $\frac{p}{n_{\mathrm{ads}}(p_0-p)} = 132\,\mathrm{mmol}^{-1} \cdot \frac{p}{p_0} - 0.7\,\mathrm{mmol}^{-1}$; b) Powder, 2.6 g: $\frac{p}{n_{\mathrm{ads}}(p_0-p)} = 13.6\,\mathrm{mmol}^{-1} \cdot \frac{p}{p_0} - 0.01\,\mathrm{mmol}^{-1}$. The error bars represent the errors due to the volume and the pressure.