FEASIBILITY OF ELECTROSTRICTION FOR MEASUREMENT OF THE CRITICAL TEMPERATURE IN THE CRITICAL VISCOSITY EXPERIMENT

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The large compressibility of a pure fluid near its critical point is a potential means of measuring the critical temperature. At the suggestion of Prof. Ferrell we observed electrostriction in xenon by applying a large voltage across a small, open capacitor immersed in the sample and then measuring the capacitance change caused by the subsequent increase in the xenon's local density. This scheme was attractive because the compressibility is a large, well–understood effect and because we were already familiar with low–voltage capacitance measurements. We found qualitative agreement with our initial expectations based on the fluid's compressibility. However, we also found an additional effect comparable in size to the expected electrostriction but proportional to the applied voltage. We have no explanation for this effect. Thus, given the Science Panel's recommendation against investing extensive effort in this direction, we are abandoning further development of an alternate means for measuring the critical temperature.

Background

Near the critical temperature T_c the compressibility χ is very large, and it is associated with the exponent γ=1.24 through the relation

$$\chi \sim t^{-\gamma} \tag{1}$$

where t is the reduced temperature. To derive the critical temperature to a precision ΔT_c from measurements of χ at a reduced temperature t near T_c, the precision $\Delta\chi$ must be

$$\frac{\Delta\chi}{\chi} \simeq \gamma \frac{\Delta T_c}{t\,T_c} = (1.24)\,\frac{(2.9\times10^{-5}\text{ K})}{(2\times10^{-6})(290\text{ K})} = 0.06\,, \tag{2}$$

where t was chosen as the reduced temperature closest to T_c where viscosity data will be acquired.

We estimated the expected density change caused by the electric field E by equating the shift in the chemical potential per unit mass μ with the change in the electrostatic energy density. In the limit of a small density change $\Delta\rho$, this is

$$\rho_c[\mu(\rho_c+\Delta\rho,T) - \mu(\rho_c,T)] = \frac{1}{2}(\epsilon_c-\epsilon_0)E^2\,. \tag{3}$$

Here, ϵ_0 is the vacuum permittivity, and ϵ_c is the permittivity of xenon at the critical density ρ_c. Using the cubic model [1] for the equation of state of xenon near its critical point, Eq.(3) becomes

$$\frac{\Delta\rho}{\rho_c} = \frac{\Gamma(\epsilon_c-\epsilon_0)E^2}{2P_c}\,t^{-\gamma}\,, \tag{4}$$

where Γ=0.058 is the amplitude of the reduced susceptibility and P_c=5.84 MPa is the critical pressure.

The Clausius–Mossotti relation connects the change in the dielectric constant to the change in density according to

$$\frac{\rho}{\epsilon}\,\frac{\partial\epsilon}{\partial\rho} = \frac{\epsilon - \epsilon_0}{\epsilon}\,. \tag{5}$$

Thus the shift ΔC in the measured capacitance is

$$\frac{\Delta C}{C_{cell}} = \left[\frac{\epsilon_c - \epsilon_0}{\epsilon_c}\right]\left[\frac{\Delta\rho}{\rho_c}\right]\left[\frac{C_1}{C_{cell}}\right]\,, \tag{6}$$

where the sensitivity of the measurement is reduced by the ratio of the fluid–filled portion of the capacitor C_1 to the total capacitance C_{cell}.

The magnitude of the electric field is constrained by upper and lower bounds. The desired signal–to–noise ratio limits the minimum allowed electric field. Very large electric fields can lead to undesirable effects such as dielectric breakdown or a shift in T_c [1].

However, a more restrictive upper bound is the requirement that the fluid's susceptibility not be significantly affected by the density change. Using the cubic model again, this limit is

$$E = \left[\frac{2aP_c}{(\epsilon_c - \epsilon_0)} \left[\frac{(\Delta\chi/\chi)}{\gamma b^2} \right]^{1/2} \right]^{1/2} t^{\beta\delta/2} = 1.3\times10^5 \text{ V/m}, \tag{7}$$

where β=0.325 and δ=4.815 are critical exponents, b^2=1.28, and a=15.4 is a cubic model parameter [1]. The numerical result for E assumed a minimum reduced temperature of $t=2\times10^{-6}$ and an allowed error of $\Delta\chi/\chi$=0.06, estimated in Eq.(2).

Measurements by others

Although sensitive capacitance measurements have been employed in pure fluids to characterize gravity–induced stratification (e.g. [2]) and to search for an anomaly in the dielectric constant (e.g. [3]), they were all low–voltage (< 20 V) techniques. We are unaware of previous measurements of electrostriction near the liquid–vapor critical point. In contrast, there are numerous reports of a "nonlinear dielectric effect" near the consolute point of binary mixtures (e.g. [4]). Most of these latter experiments made use of a rapid pulse technique, inappropriate for our expected long equilibration times. The theory associated with the binary mixture measurements is based on induced anisotropy of the concentration fluctuations [5]. However, when we applied the predictions [6] of this model to xenon we found a negligible effect in comparison to electrostriction. Therefore, other than our use of the cubic model equation of state, we received little guidance from theory and previous experiments.

Apparatus

There were several constraints in the capacitor's design. First, the gap containing the xenon between the capacitor's plates needed to be small to avoid problems with long thermal relaxation times. Second, the capacitor needed to be small enough to be added to the existing viscometer. Third, the capacitor needed to be mechanically stable and made out of materials unlikely to contaminate the xenon. Our design, indicated in Fig. 1, consisting of a sandwich of copper and glass soldered together with indium, met all three requirements. The gap size was determined by the 0.18 mm thick glass spacers (microscope cover slips), and other dimensions of the capacitor were near the limit of easy manual construction.

Our measurements made use of a cylindrical cell similar to that described in the Science Requirements Document. The screen oscillator and its associated electrodes were not present. Instead, a tuning fork mixer (unused in these tests) and the capacitor were placed into positions determined by their attachments to electrical feedthroughs located at the end of the cell. The cell was filled to within 0.3% of the critical density. Weighing showed that less than 0.03% of the sample leaked out over the next 46 days.

Two circuits were used to measure the cell's capacitance while applying a DC bias voltage. We first used a circuit, shown in Fig. 2, similar to that used for the oscillating screen. Problems with the stability of the reference capacitor and the 10 kHz oscillator prompted the use of a commercial capacitance bridge and a synthesized 10 kHz source, indicated in Fig. 3.

Technique

We considered two methods for locating T_c in the low–gravity experiment. The simplest would be to maintain a large voltage across the capacitor and observe the "signature" of capacitance changes associated with crossing T_c. Slow systematic errors such as drift of the electronics would be unimportant provided the capacitance signal changed sufficiently rapidly near T_c. Unfortunately, because of the planned minimum ramp speed of 3×10^{-8} K/s and the complicating effects of equilibration in the capacitor gap very close to T_c, we have no theory to reliably associate T_c with the observed signature to the desired precision of 29 μK.

The second method would avoid the equilibration problem by using capacitance measurements made only at 0.6 mK and more above T_c. The required extrapolation places a greater burden on the measurement's accuracy, indicated by Eq.(2) above. Obtaining the required accuracy would be eased by the use of a difference method, namely observing the change in capacitance following a change in the bias voltage, after allowing sufficient time for equilibration.

The thermal time constant associated with density relaxation in the capacitor gap following a change in the electric field can be calculated from xenon's thermal diffusivity D_T and the gap size $2x_0$. For example, at 1 mK above T_c,

$$\tau = \frac{x_0^2}{\pi^2 D_T} = \frac{(9\times10^{-5}\ \mathrm{m})^2}{\pi^2(6\times10^{-12}\ \mathrm{m\cdot s^{-2}})} = 1.4\times10^2\ \mathrm{s}\,, \tag{8}$$

compatible with the time of a viscosity measurement. Eq.(8) assumes a reduction in τ by the factor of four applicable to closed, effectively one–dimensional systems near the critical point [7]. A better estimate would require a more careful accounting of thermodynamics in the presence of an inhomogeneous electric field [8].

Electrical parameters and the signal–to–noise ratio.

With the bridge of Fig. 3 driven at 10030 Hz at five to ten volts amplitude, the lock–in gain was typically set to give an output sensitivity of one to three kV/pF. The measured total capacitance was typically C_{cell}=25.4 pF. The bridge's dissipation setting depended much more strongly on frequency than on temperature. The equivalent parallel resistance was 2×10^8 ohms at 10 kHz, but this increased linearly to 8×10^9 ohms at 100 Hz (compatible with "DC" measurements of $\geq2\times10^{11}$ ohms).

The circuit's output wandered slowly under typical operating conditions. As a result there was a roughly "1/f" noise spectrum below 5 Hz. Above 5 Hz the noise was limited by the lock–in's preamp to 2×10^{-6} pF/Hz$^{1/2}$. We observed similar behavior when measuring a fixed silver mica capacitor at room temperature.

We do not know the source of the low–frequency noise. One possibility considered was the temperature dependence of the capacitance bridge, rated at less than 5×10^{-6} K^{-1}. However, the noise observed at 0.1 Hz would then correspond to temperature noise in the bridge's 100 pF standard of at least 4×10^{-3} K/Hz$^{1/2}$.

Relaxation following a change in the bias voltage

Using the circuit of Fig. 2, we observed the evolution of the apparent capacitance following a change in the bias voltage. At 19 and 48 mK above T_c we observed relaxation characterized by time constants in the range of five to ten seconds, consistent to within a factor of two with calculations using Eq.(8). At 98 mK above T_c, very little relaxation was seen on this time scale.

We also found unusually slow relaxation behavior at all temperatures. This unexplained behavior was characterized by a 10^{-4} pF drift over several hundred seconds in the same direction as the "proportional effect" described below.

<u>Low–voltage measurements of capacitance vs. temperature</u>

Fig. 4 plots our measurements of capacitance as a function of temperature. Above T_c the relative change of 3.4×10^{-4} K^{-1} was about 10 times larger than expected from the thermal expansion of the capacitor. Below T_c the data were fit by a function incorporating the known coexistence curve of xenon and the free parameters T_c and C_1, the fluid portion of the capacitor. We found T_c=16.655±0.005 °C and C_1=3.14±0.01 pF, where the errors were estimated from fits optimized through trial and error.

<u>Measurements of capacitance vs. voltage</u>

The electrostriction measurements were complicated by an unexpected apparent capacitance change proportional to the applied bias voltage and whose sign depended on the "polarity" of connections made to the cell. This can be seen in the typical data of Fig. 5 taken at 48 mK above T_c. Most of this "proportional effect" took place within one second. A much slower, subsequent drift, proportional to the voltage change, was also seen. Both effects hindered our efforts to unambiguously measure the electrostriction.

Fig. 6 shows the temperature dependence of the proportional effect. The effect remained when the capacitor was removed and measured in air.

Fig. 7 shows measurements of the observed "quadratic effect", believed to be caused by electrostriction. The proportional effect was removed by using the average of measurements taken at bias voltages of +150 V and –150 V. A calculation of the expected capacitance change is also plotted. For the calculation, which relied on no free parameters, we used the values of C_1 and T_c found from the two–phase measurements. The dominant uncertainty, the capacitor gap d, is indicated by the two curves calculated with the values d=0.16 and 0.18 mm.

The calculated curve describes the data only qualitatively. We neglected the effects of density stratification close to T_c, and the errors close to T_c are of the same sign as expected from such neglect. Far from T_c the errors are 2×10^{-4} pF or smaller, though much greater than the expected values. Because of its comparable size, the unexplained proportional effect may be the source of these latter errors.

<u>Further work</u>

No further work on electrostriction is planned. The encountered technical problems, in particular the proportional effect and the associated slow drift following changes in the bias voltage, prevent the accurate location of T_c with the present apparatus. Assuming these effects were due to an unintended asymmetry in the capacitor, they could be eliminated by a different choice of capacitor materials or by an improved cleaning technique.

We also considered the use of a large AC bias voltage as a means of eliminating the proportional effect. Use of the capacitance bridge's 10 kHz drive voltage for this purpose would require addressing the possible effects of electronic crosstalk and of detector nonlinearity. In any case, the proportional effect seen with DC bias voltages must be either reduced or understood sufficiently to trust the results of measurements made with AC bias voltages.

After demonstrating the accuracy of electrostriction measurements for locating T_c, the device could be incorporated into the viscometer only after proving that it would not interfere mechanically or electrically with the viscosity measurements.

References

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Figures

1. The electrostriction capacitor. It was fixed in a plane tilted about 30° from vertical with one open end near the cell's midline.

2. The circuit used to observe the electrostriction time constant.

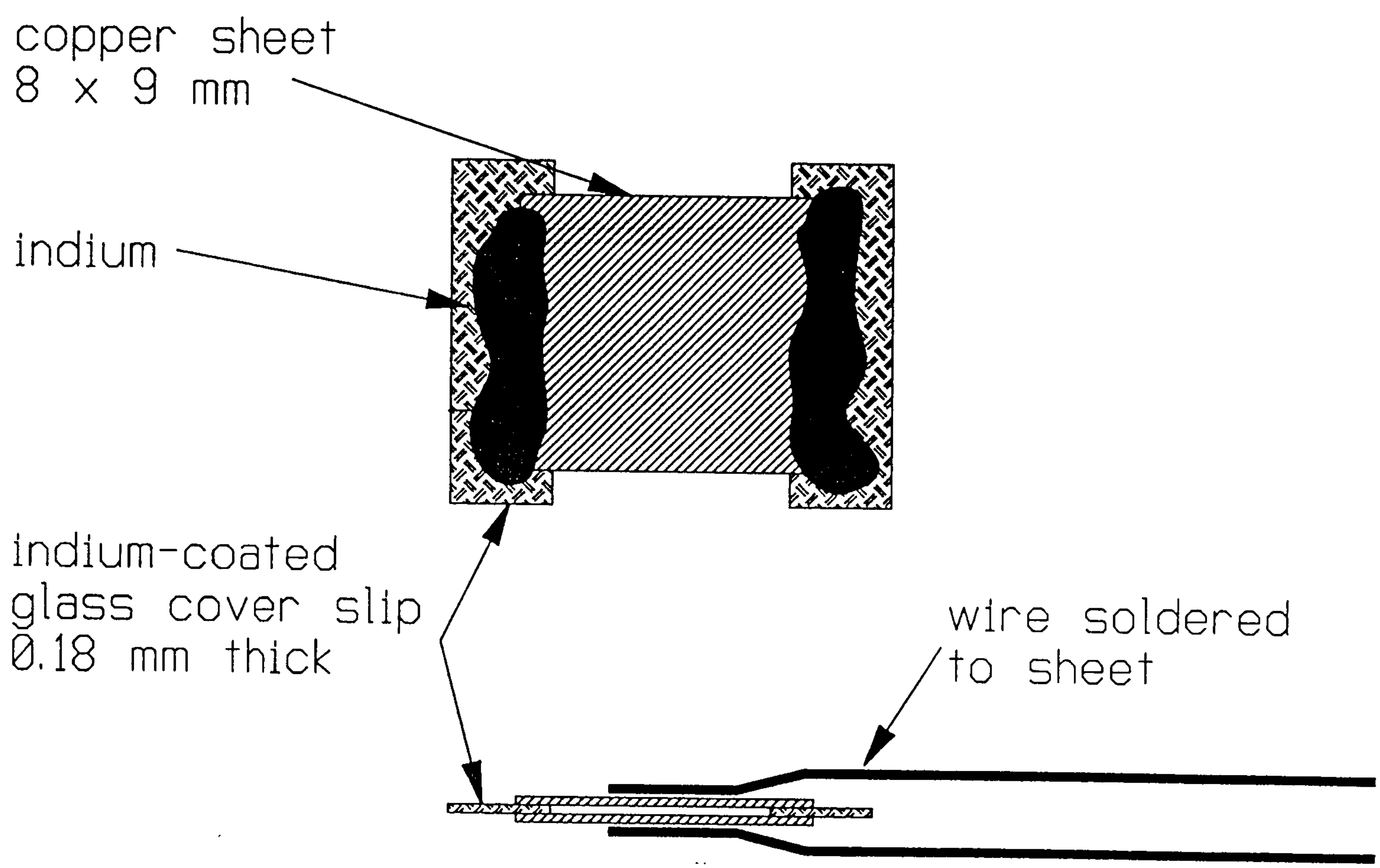
3. The circuit used for most of the electrostriction measurements relied on a General Radio model 1615 capacitance bridge.

4. Low–voltage measurements of the capacitance as a function of temperature. The slope above T_c was about 10 times greater than expected from the thermal expansion of copper. The temperature dependence below T_c could be described by the known liquid and vapor densities of saturated xenon.

5. Observed changes of the capacitance from an arbitrary zero. Note the expected quadratic shape is modified by an additional "proportional effect". The scatter in the data reflect ambiguity caused by slow drift associated with the proportional effect.

6. The size of the the proportional effect. Although it depended on temperature, it was present even after xenon was removed from the cell (not shown).

7. The magnitude of the electrostriction effect, defined from the average of the measurements at –150 V and +150 V. The curves are calculations, with no free parameters, of the expected amplitude. The main uncertainty is the capacitor gap d, defined by the 0.18 mm thick glass spacers. Far from T_c the measurements are complicated by the presence of the proportional effect and its associated drift. The complications of gravity–induced stratification close to T_c were not included in the calculation.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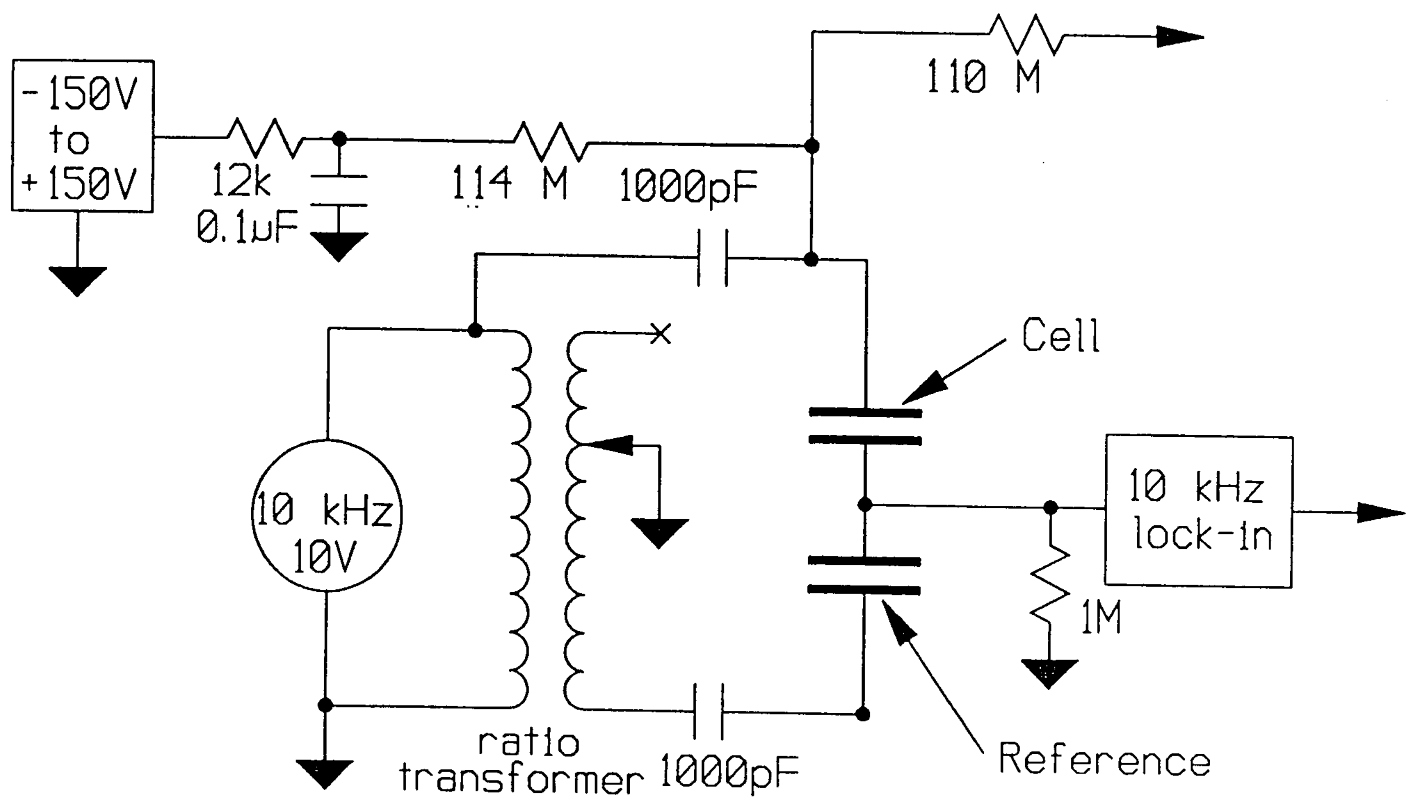
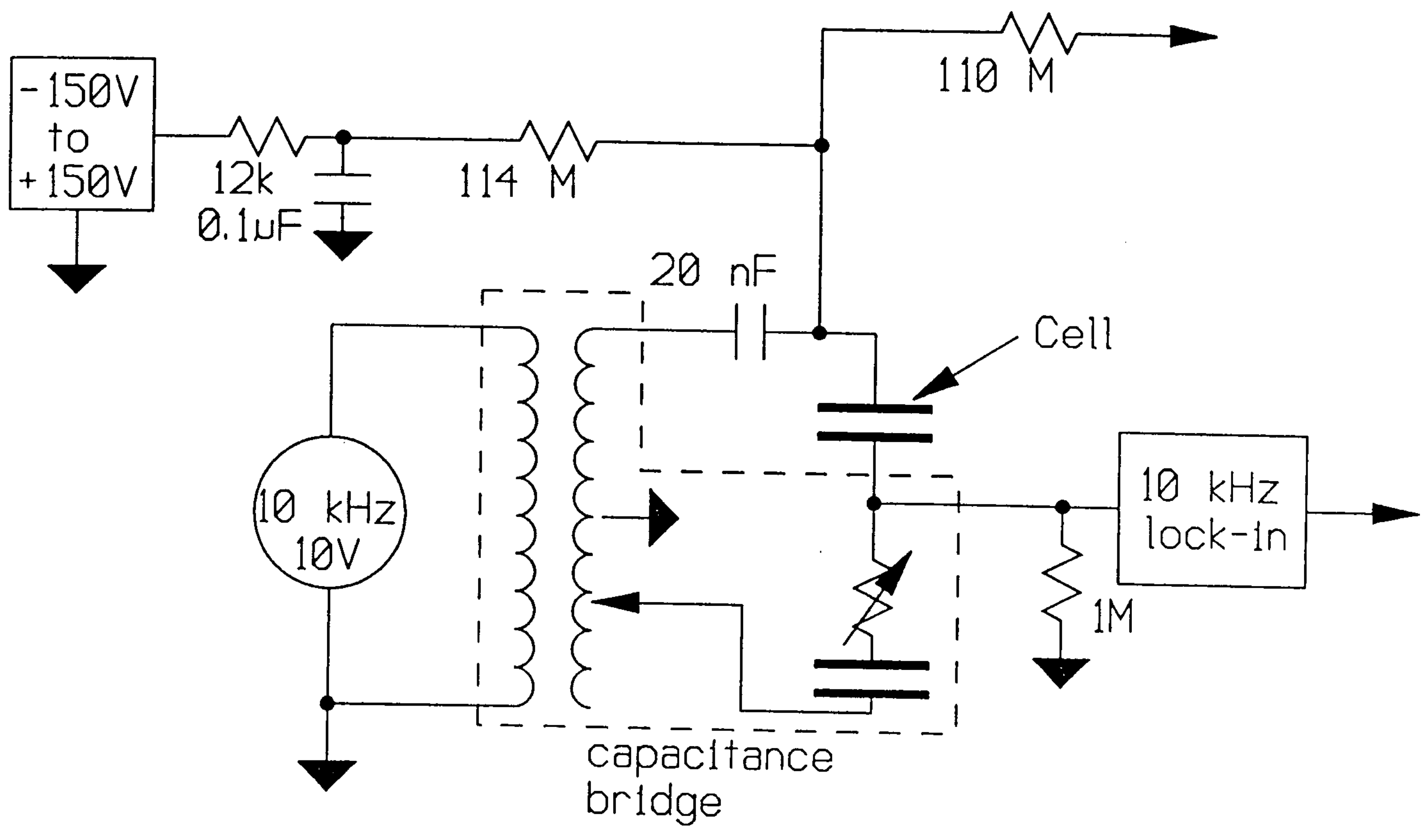
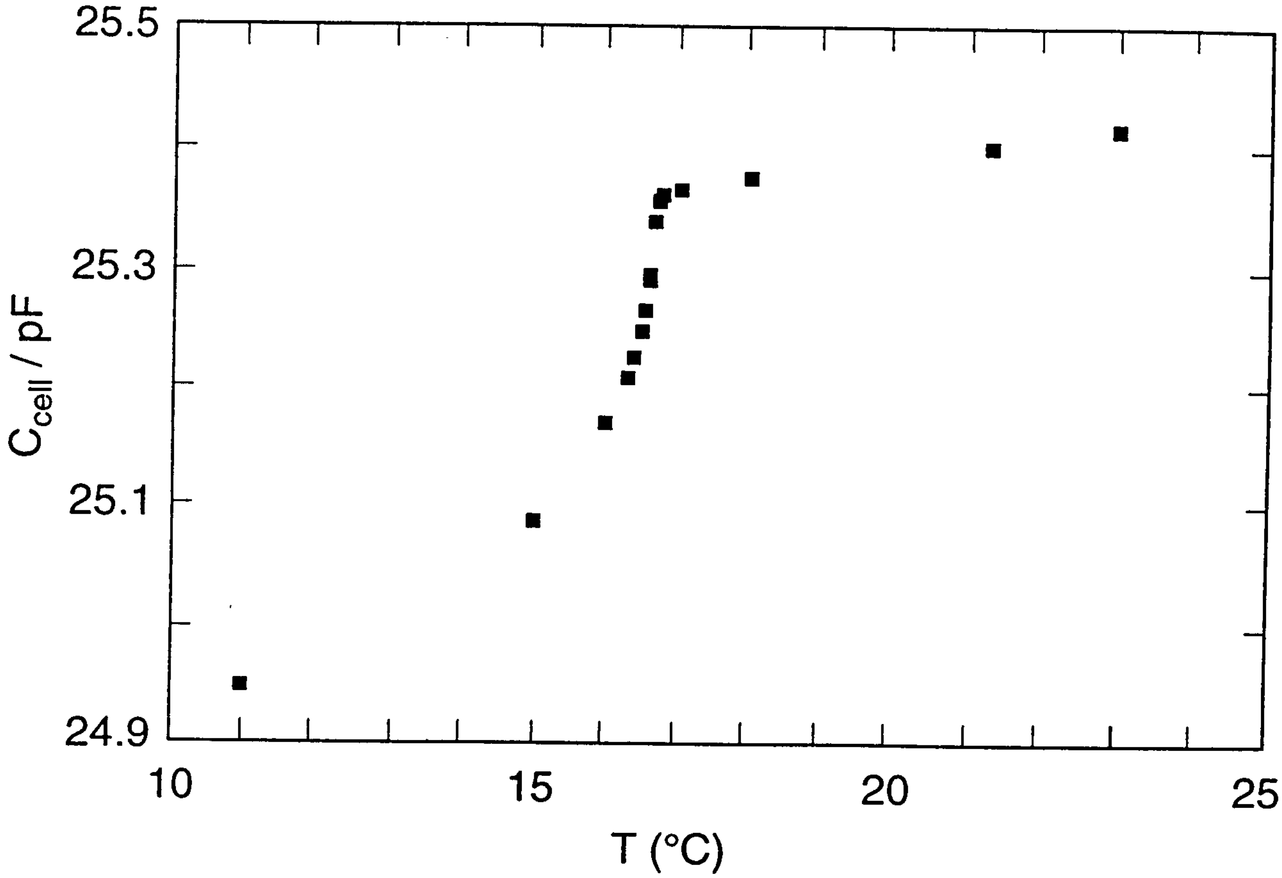
indium
indium-coated
glass cover slip
0.18 mm thick
wire soldered
to sheet

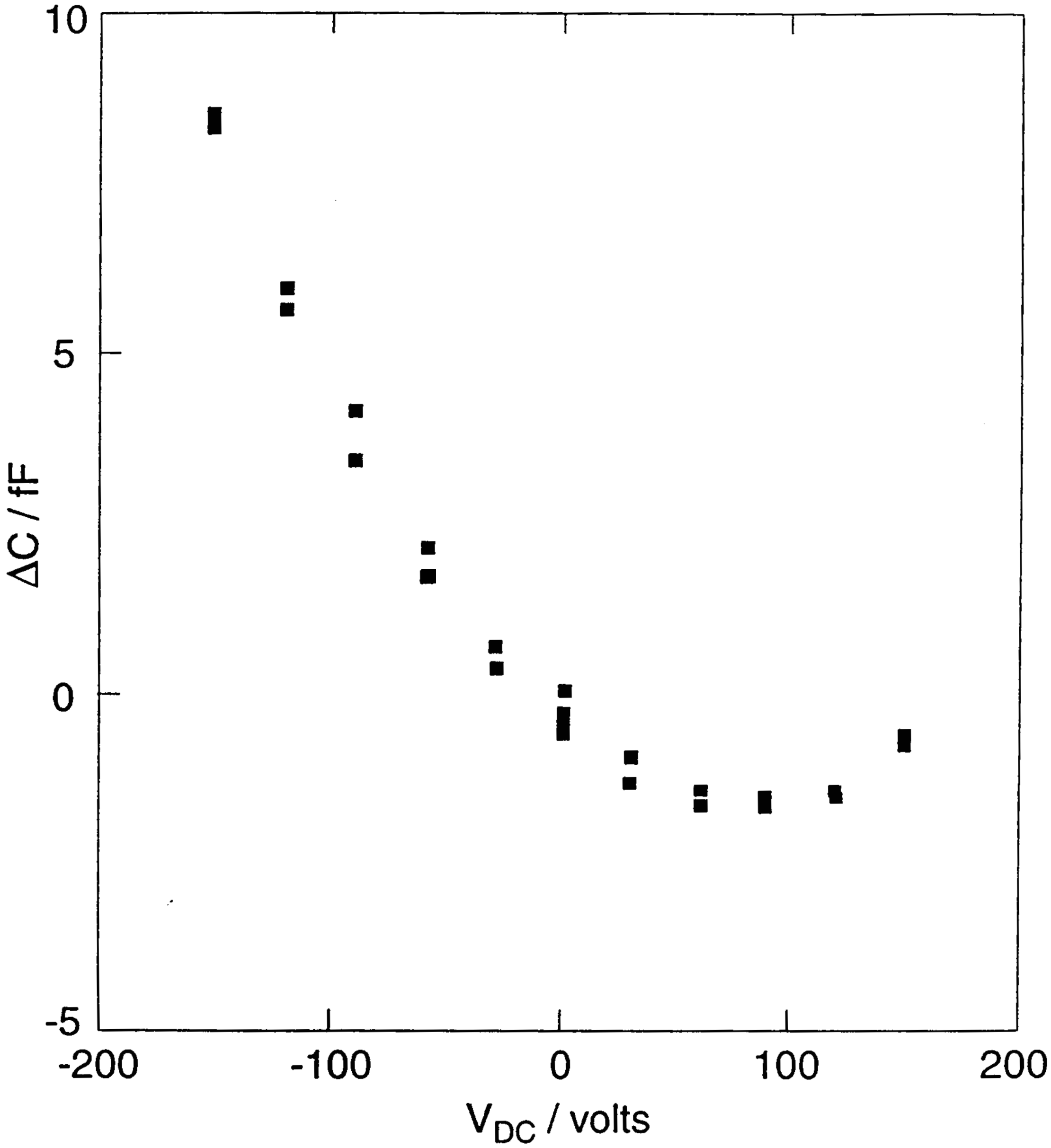


-150V
to
+150V
12k
0.1µF
114 M
1000pF
110 M
Cell
10 kHz
10V
ratio
transformer
1000pF
Reference
1M
10 kHz
lock-in

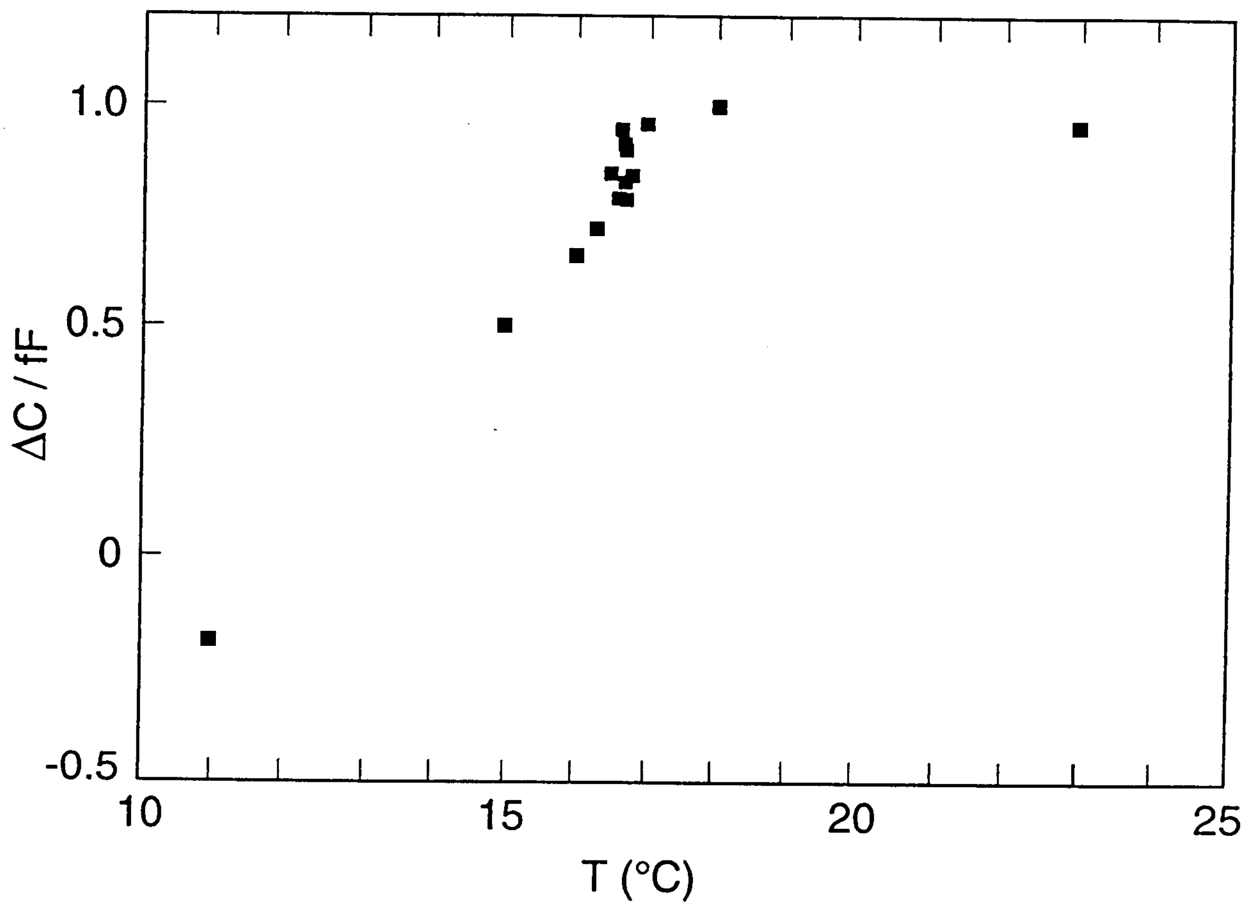

-150V
to
+150V
12k
0.1uF
114 M
110 M
20 nF
Cell
10 kHz
10V
10 kHz
lock-in
1M
capacitance
bridge

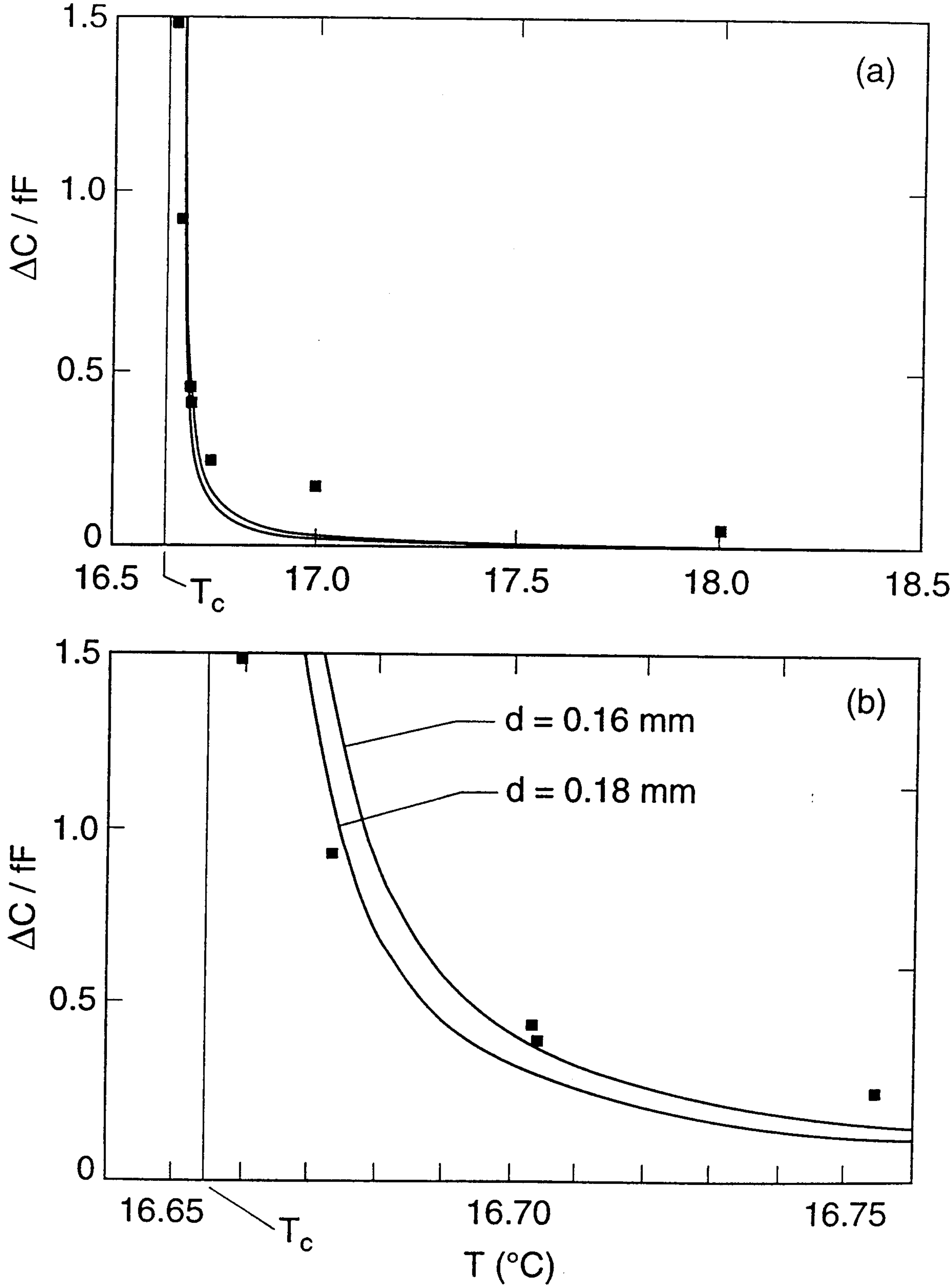


25.5
25.3
25.1
24.9
C_{cell} / pF
10
15
20
25
T (°C)



10
5
0
-5
ΔC / fF
-200
-100
0
100
200
V_DC / volts


1.0
0.5
0
-0.5
ΔC / fF
10
15
20
25
T (°C)


(a)
ΔC / fF
1.5
1.0
0.5
0
16.5
17.0
17.5
18.0
18.5
T_c
(b)
d = 0.16 mm
d = 0.18 mm
ΔC / fF
1.5
1.0
0.5
0
16.65
16.70
16.75
T_c
T (°C)