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FILMS AT HIGH HYDROSTATIC PRESSURE

by

B. A. Newman, K. T. Chung, K. D. Pae and J. I. Scheinbeim

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Abstract

The pressure dependence of the piezoelectric hydrostatic pressure coefficient, d_p, and the pyroelectric coefficient, p_y, was determined from atmospheric pressure to 7 Kbar over a temperature range from $-80°C$ to $+48°C$ for poled, uniaxially oriented film. The effect of the glass transition on d_p and p_y as a function of pressure is compared to the pressure dependence of the glass transition temperature obtained from dielectric studies. The ratio of d_p/p_y as a function of pressure and temperature is presented.

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Introduction

Many recent investigations have been concerned with the origin of the piezoelectric and pyroelectric properties of poled poly(vinylidene fluoride) (PVF$_2$) films. Various mechanisms for the observed phenomena have been suggested, including bulk polarization due to switching of molecular dipoles in the polar crystals,[1,2] non-uniform charge injection leading to asymmetric distribution of real charge in the film,[3] field induced charge trapping of injected charge or ionic charges present as impurities.[4] Other suggestions such as a reversible temperature dependence of the crystallinity[5] and metal-polymer interfacial phenomena[6] have been proposed as possible contributing mechanisms.

A detailed theoretical model proposed by Broadhurst[7] et al, assumes that PVF$_2$ crystals are ferroelectric and that the direction of polarization of polar crystallites can be changed by field. Thus, poling produces a remnant polarization, P$_o$, which changes as a result of changes in temperature (pyroelectricity) or applied stress (piezoelectricity). Although it is now established that this theory can account largely for the observed phenomenon, it is possible that other mechanisms may play a role in certain cases. PVF$_2$ is known to be a semicrystalline polymer consisting of lamellar crystals in an amorphous matrix. Further studies are required in order to gain further insight into the relationship between structure and morphology and the electrical properties. R. G. Kepler and R. A. Anderson[8] were able to account for only one-half of the total pyroelectricity on the basis of secondary pyroelectricity. They were unable to detect any

appreciable contribution from primary pyroelectricity and suggested that a large contribution arose from a reversible temperature dependence of the crystallinity.[7] Other suggested mechanisms may also be important. In order to clarify these problems data is needed across a wide range of temperature and pressure. Of particular interest is the effect of the glass transition temperature T_g.

No studies have been made at high pressures and only a few investigations have been made over a wide enough temperature range to include the T_g. Buchman[2] found a decrease in the pyroelectric effect with increasing temperature for PVF_2 in the glassy state, while Burkard and Pfister[9] observed a small increase which they related to the glass thermal expansion. The latter observers also noticed a small discontinuity in slope for the pyroelectric coefficient at $T = +20°C$. Ohigashi[10] determined the variation of several piezoelectric constants (d_{33}, e_{33}, d_{31}, e_{31}, d_{32}, e_{32}) with temperature from $-170°C$ to $+100°C$ at high frequencies, $20KH_z$ to $30MH_z$. Furukawa, Aiba and Fukada[11] determined the variation of both real and imaginary components of e_{31} with temperature from $-150°C$ to $+100°C$ at $10H_z$. In both studies an increase in e_{31} to a maximum value followed by a decrease was observed. The temperature at which the maximum occurred differed by ~80°C in the two studies probably because of the difference in frequencies used.

A comparison of piezoelectricity and pyroelectricity over a large range of temperature and pressure provides an indication of whether both phenomena originate from a common source. The pyroelectric constant P_y can be defined:

$$P_y = \frac{d(Q/A)}{dT} \bigg)_{E = 0}$$

where $\frac{d(Q/A)}{dT}$ is the rate of change of surface charge density with temperature. The hydrostatic pressure coefficient can be defined

$$d_p = \frac{d(Q/A)}{dP} \bigg)_{E = 0}$$

where $\frac{d(Q/A)}{dP}$ is the rate of change of surface charge density with pressure. If $\frac{d(Q/A)}{dT}$ and $\frac{d(Q/A)}{dP}$ only originate from dimensional changes we have

$$P_y = (\frac{\alpha}{s}) \, d_p$$

where α is thermal expansion coefficient and s is the compliance.

We have determined d_p and P_y at pressures up to 7.0 Kbar and in a temperature range from -80°C to + 48°C. The pressure and temperature dependence of P_y has been reported elsewhere[12] but are presented again here to provide a good comparison with the piezoelectric data.

Experimental

Poled, uniaxially oriented PVF_2 films (piezofilm - obtained from Kureha Company) were used. Piezoelectric, pyroelectric and other physical properties of the film are listed in Table 1. X-ray diffraction photographs showed that the crystal structure was phase I and that the film was highly oriented (C-axis in the draw direction.

The high pressure electrical call is described in a separate publication.[12] It consists of a thick-walled cylinder which could be pressurized up to 7.0 Kbar and contained an internal heater which, used in conjunction with external cooling using liquid nitrogen, permitted excellent temperature stability and controlled heating and cooling down to ~ -196°C.

In the measurement of the hydrostatic piezoelectric coefficient (d_p), the same procedure was used at all temperatures and pressures. The sample was first heated to the required temperature (T_o) and then pressurized to a constant pressure (P_o). The electrodes were then short-circuited at the new temperature and pressure until the sample was completely relaxed. The pressure was then increased slowly in 0.05 Kbar steps up to a pressure $P = P_o + 0.5$ Kbar. The change in surface

charge Q produced by the application of pressure was measured using an electro-meter (Keithley model - 616) in the charge mode. We adopted an operational definition

$$d_p = \frac{1}{A_o} \left(\frac{\delta Q}{\delta P}\right)_{E = 0}$$

where A_o is the initial area. In the plot of integrated charge Q versus pressure, the initial slope at P_o was used to determine d_p.

The same value for d_p was found using either increasing or decreasing pressures. Since abrupt changes in pressure can introduce change in temperature (for a constant volume cell) small changes in polarization could arise from the pyroelectric effect. We determined the maximum error due to this effect to be ~3%.

The pyroelectric data reported here was obtained using the same electrical cell and varying temperature (as opposed to pressure). The experimental procedure is presented in a previous publication.[12]

Since measurements were made over a wide range of pressure and temperature, the film could be in the glassy state either because of the low temperature or the high pressure. The pressure dependence of the glass transition temperature was determined by connecting the electrodes to a commercial device (Toyo Seiki Piezotron) and measuring the dielectric loss, ε'', at 3 H_z. The maximum in ε'' obtained by ramping temperature up and down through the glass transition region was assumed to correspond to T_g.

Results and Discussion

Fig. 1 shows the pressure dependence of d_p at various temperatures from -48°C to +48°C. d_p decreases with increasing pressure at all temperatures, the most rapid decrease occurring at the lowest pressure and highest temperature. At room temperature the decrease is ~ 25% over the first 1 Kbar. The isotherm

at 24°C shows some discontinuity in slope at ~ 5.0 Kbar. This discontinuity is also evident in the lower temperature isotherms but shifted to lower pressures. We attributed this to the pressure induced glass transition P_g, which at 24°C occurs at ~ 5 Kbar. For temperatures below -48°C, d_p decreases smoothly with pressure, which would be expected since the polymer is in the glassy state over the entire range. At temperatures above 48°C, P_g is greater than 7.0 Kbars and so the variation of d_p with pressure is also smooth. It is interesting that the change is d_p as the pressure induces a change from the rubbery to the glassy state is so small. The pressure dependence of P_y showed a similar behavior and is shown in Fig. 2.

Fig. 3 shows the temperature dependence of d_p at various pressures up to 7.0 Kbars. For comparison, Fig. 4 shows the temperature dependence of p_y at various pressures. The immediate impression is that both d_p and p_y show the same general dependency. At atmospheric pressure, below ~ 55°C both d_p and p_y decrease slowly with increasing temperature; above this temperature both constants increase rapidly up to +48°C with some change of slope at ~ 20°C. The effect of pressure is to shift this general dependency to higher temperatures.

The minimum in d_p and p_y (observed at ~ 55°C) at atmospheric pressure is very close to the glass transition temperature for PVF_2. In Fig. 5 the pressure dependence of the glass transition temperature $T_g(P)$ of the film is shown. This data was determined from the dielectric loss spectrum obtained at various pressures up to 7.0 Kbar. The temperature at which the minimum of d_p occurs is shown plotted on the same figure. The curves run closely parallel to each other suggesting similar origins. The constant difference in absolute temperature between the two curves is quite reasonable considering the difference in technique used. In fact the values obtained from d_p and p_y measurements are very close to values of T_g determined by dynamic mechanical[13] and other tests.

The high temperature anomaly (~ 20°C at atmospheric pressure) is more pronounced at the highest pressures. The pressure dependence if the transition temperature (which we will call T_t) is less than that of T_g and so at the highest pressures these two transitions approach each other.

The transition temperatures T_g and T_t divide the temperature dependence of d_p and p_y into three regions; below T_g, from T_g to T_t, and above T_t. Below T_g, p_y appears to decrease steady with increasing temperature, while d_p shows a shallow maximum with a slight decrease just before T_g. More recent measurements taken at lower temperatures indicate that p_y also exhibits a shallow maximum at temperatures below -90°C. Buchman[2] also observed a decrease in p_y for PVF_2 in the glassy state although this was not observed by Burkard and Pfister.[9] The decrease in p_y is small, ~ 0.1 nc/cm^2 from -82°C to -48°C, but is observed at all pressures. We have no satisfactory explanation for this at the present time. Both thermal expansion, compressibility and the greater librational motion of chains at higher temperatures would lead to steady increases in d_p and p_y with temperature. Present theories of pyroelectricity and piezoelectricity appear unable to adequately explain the observed behavior of PVF_2 in the glassy state.

Between T_g and T_t both d_p and p_y increase rapidly at first and then level off as the temperature approaches T_t. At higher pressures this gives rise to a plateau region. A similar behavior was also observed by Burkard and Pfister although not by Buchman. Volumetric analysis of PVF_2 resin crystallized in the phase II form shows a T_g at -52°C and another higher temperature relaxation at about 13°C.[14-16] Dynamic mechanical tests also show a loss peak ~ 20°C.[13] It has been suggested that this transition is related to morphological features.[14] Further studies are required to clarify this phenomenon, but in any event the change in temperature dependence of both p_y and d_p appear to be related to this relaxation.

Figs. 6a and 6b show the ratio of d_p/p_y at various high pressures and temperatures from -84°C to +48°C. Theoretical studies predict that the ratio should be ~ 5.0 x 10^{-3} $cm^2/K/N$.[16] This is in agreement with results obtained at atmospheric pressure and temperature and implies that both d_p and p_y result only from dimensional changes or

$$p_y = \frac{\alpha}{s} d_p$$

Figs. 6a and 6b show that the ratio varies with temperature and pressure from ~ 3.0 x 10^{-3} cm^2°K/N to ~ 9.0 x 10^{-3} cm^2°K/N. Further experimental studies of α and s are needed to determine their temperature and pressure dependence and these are being carried out at the present time. For pressures up to 2.0 Kbar, d_p/p_y increases in absolute value with temperature in the glassy state. Above T_g the ratio drops until T_t is reached when it begins to increase again. At 3.0 Kbars a very rapid decrease in d_p/p_y occurs at the glass transition from 8.9 x 10^{-3} to 5.7 x 10^{-3} as the temperature increases 12°C. At higher pressures T_g and T_t are too close to resolve individual responses. It is interesting to note that at the highest temperature, 48°C, the ratio d_p/p_y varies only from 4.55 x 10^{-3} to 5.05 x 10^{-3} at all pressures.

Acknowledgment

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Table 1

Physical Properties of Piezofilms

Piezoelectric Strain Coefficients $(10^{-12} C/N)$	d_{31}	22.3	$(3H_z)$
	d_{32}	2.0	$(3H_z)$
Piezoelectric Stress Coefficients $(10^{-2} C/m^2)$	e_{31}	6.75	$(3H_z)$
	e_{32}	0.43	$(3H_z)$
Elastic Moduli			
Parallel to draw direction $(10^9 N/m^2)$	C_{11}	3.71	$(3H_z)$
Perpendicular to draw direction $(10^9 N/m^2)$	C_{1}	1.46	$(3H_z)$
Dielectric Constant	E	12.3	$(3H_z)$
Pyroelectric Coefficient $(10^{-9} C/cm^2 K)$	P_y	3.0	$(1.75K/min)$

FIGURE CAPTIONS

Fig. 1 – The pressure dependence of d_p at different temperatures

Fig. 2 – The pressure dependence of p_y at different temperatures

Fig. 3 – The temperature dependence of d_p at different pressures

Fig. 4 – The temperature dependence of p_y at different pressures

Fig. 5 – The pressure dependence of T_g and d_p (minimum)

Fig. 6a – The pressure dependence of d_p to d_y (0-4 Kbar)
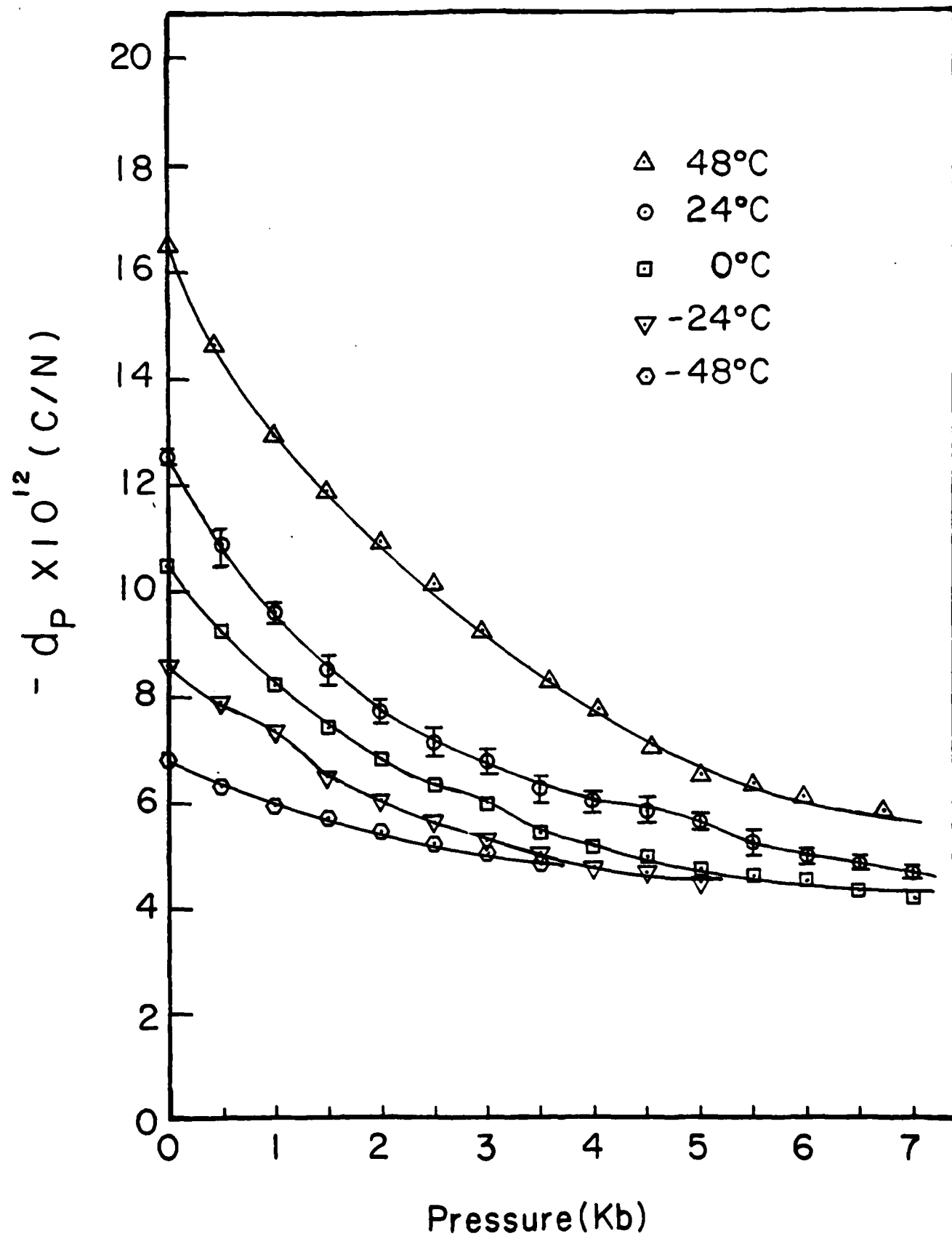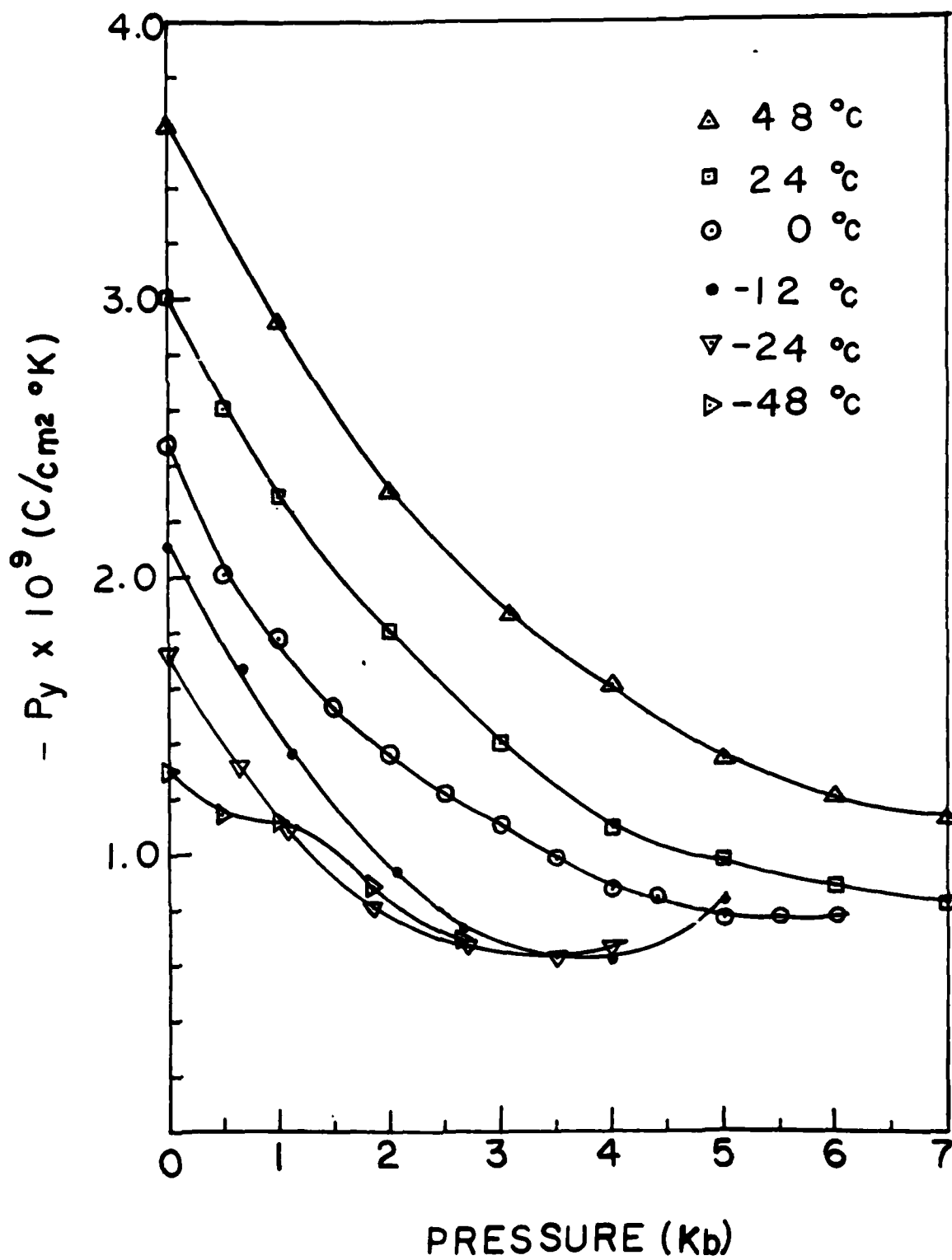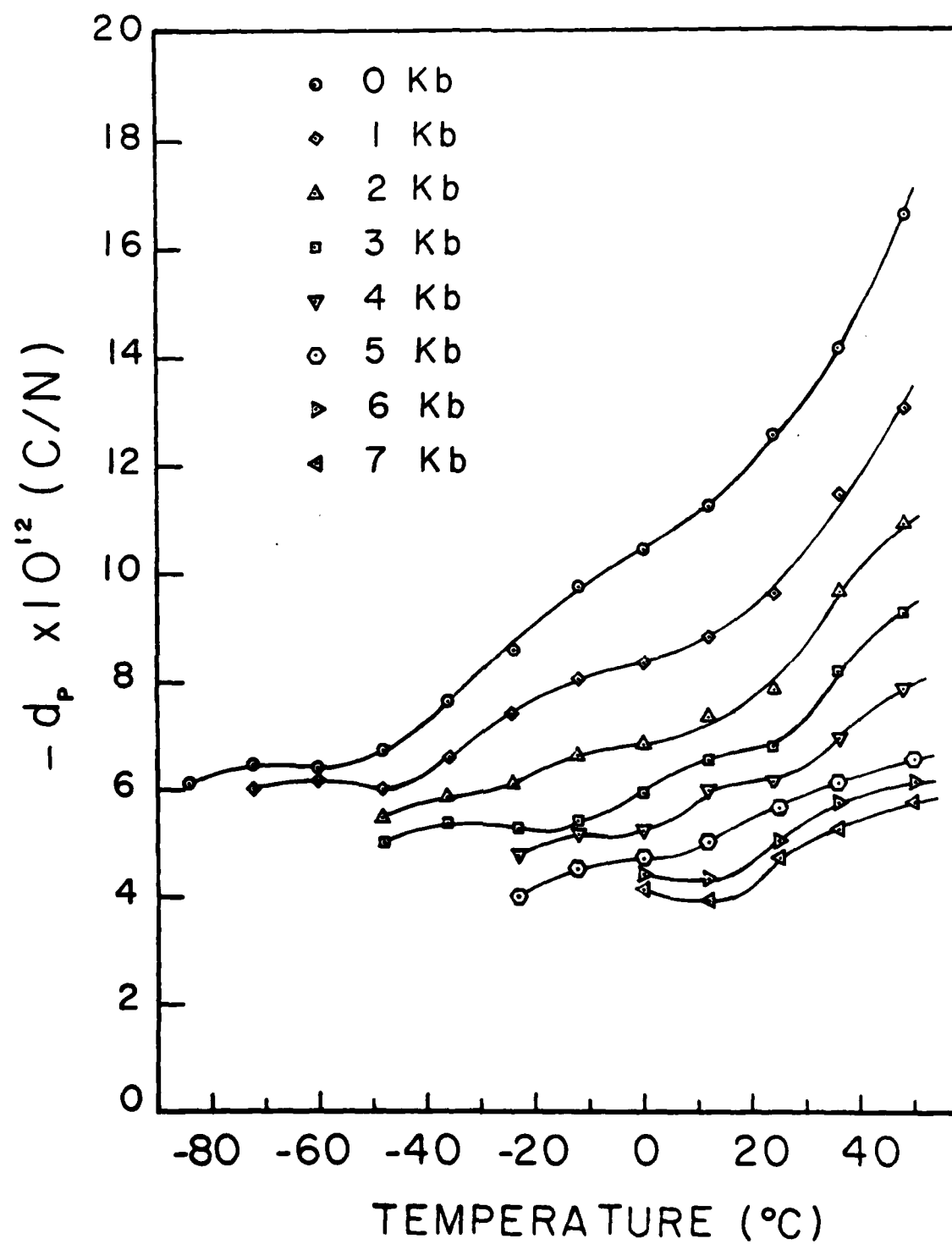
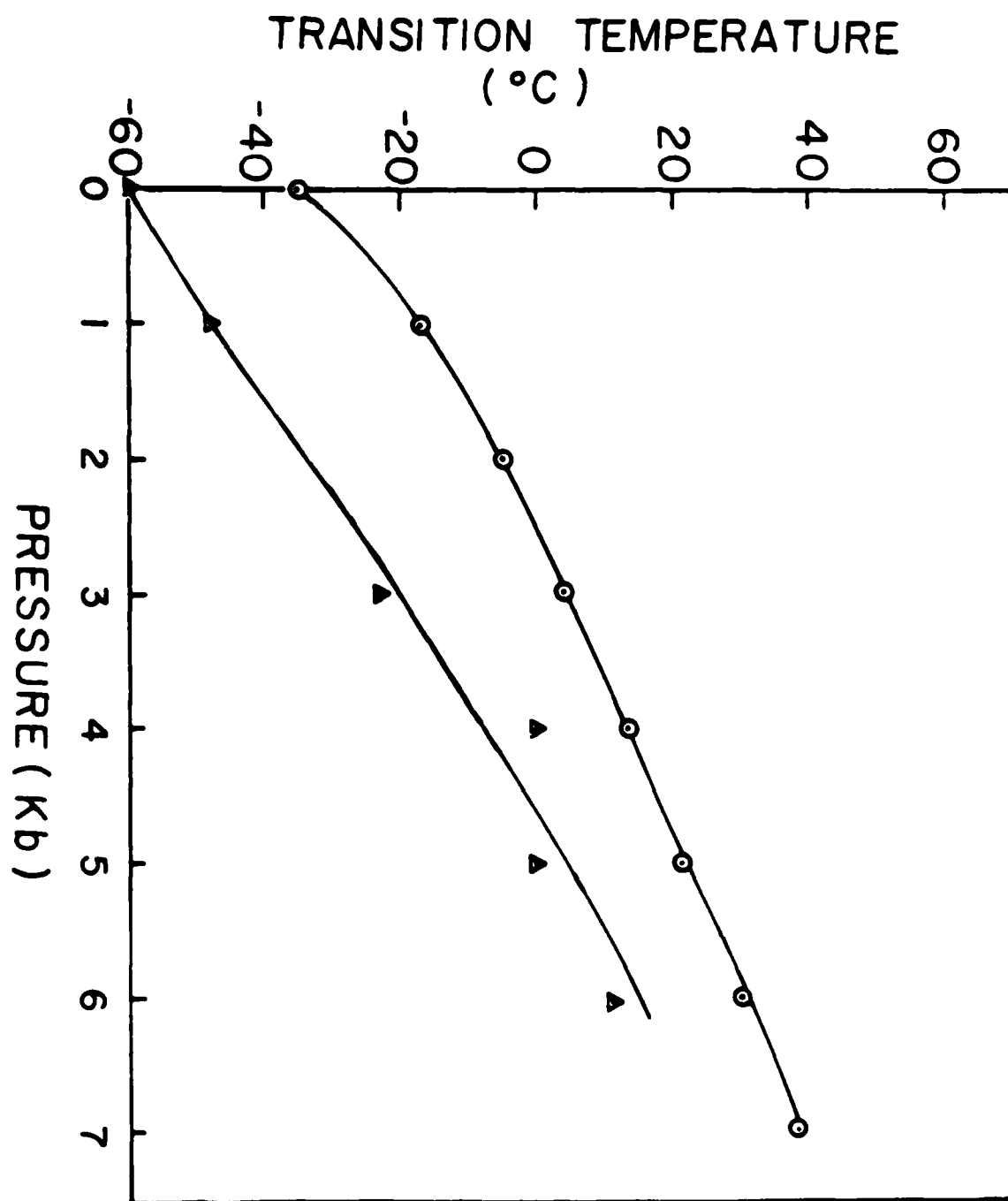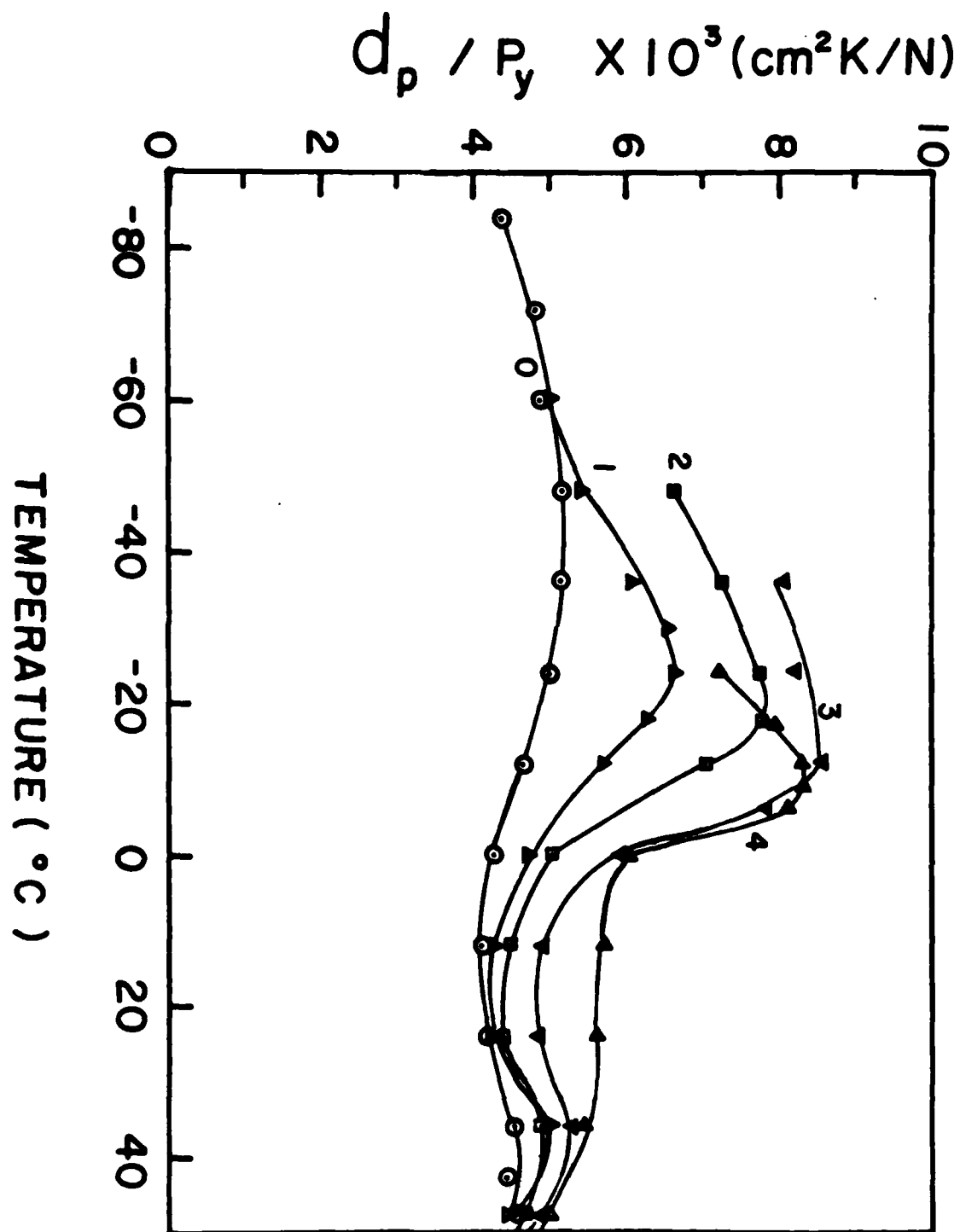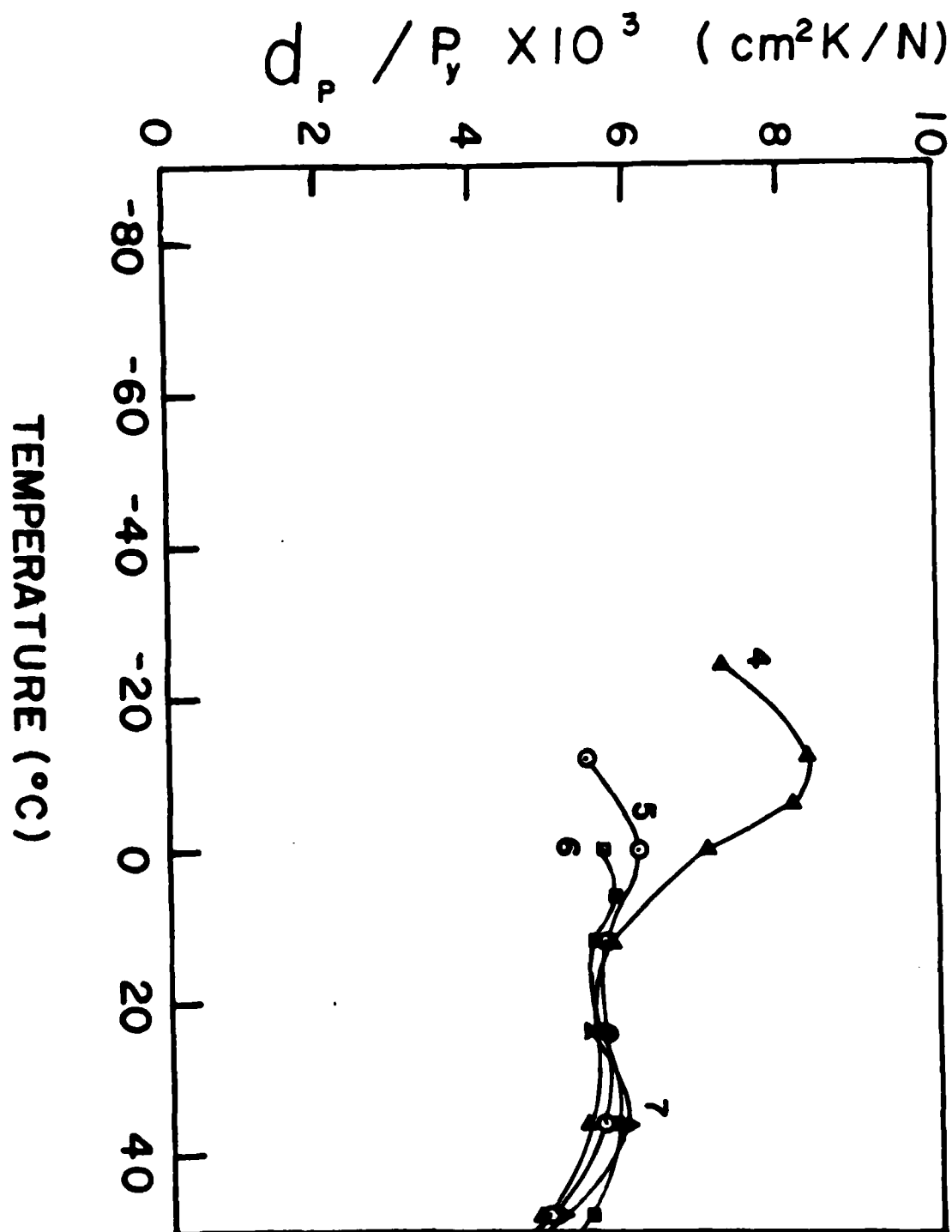Fig. 6b – The pressure dependence of d_p to d_y (4-7 Kbar)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6a

Figure 6b

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