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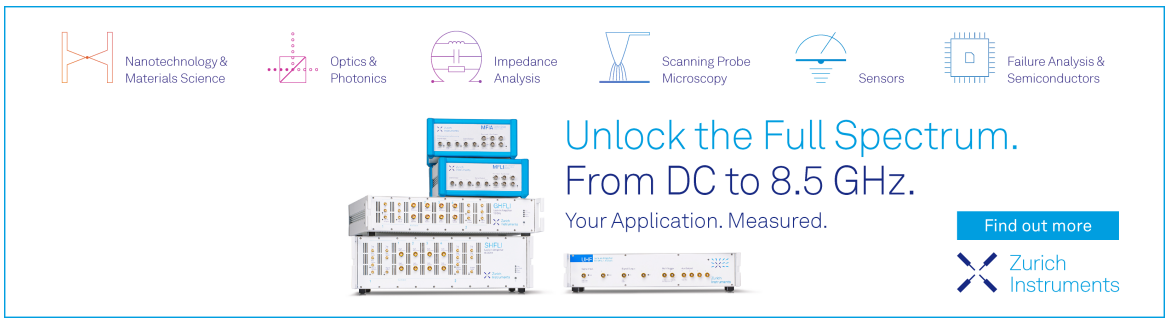
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Thermoelastic temperature changes in poly(methyl methacrylate) at high hydrostatic pressure: Experimental

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Temperature changes as a result of large rapid hydrostatic pressure changes were measured for poly(methyl methacrylate) at various temperatures from ambient to 95 °C and for various pressure increments from 14 to 207 MN/m^2. We observe complete reversibility of the measurements over the pressure range studied. The value of the incremental ratio $\Delta T/\Delta P$ was a function of both temperature and pressure, ranging from 0.04 to 0.09 K/MNm^{-2} from 298 to 368 K at low pressures, and 0.03–0.05 at 200 MN/m^2 over the same temperature range. The largest variation of $\Delta T/\Delta P$ with pressure was at low pressures, the ratio becoming nearly constant above about 200 MN/M^2.

PACS numbers: 36.20. − r, 64.30. + t, 65.70. + y, 65.50. + m

INTRODUCTION

The thermoelastic effect in polymers is primarily associated with force-temperature measurements at constant elongation[1,2] and is most commonly recognized by the well-known phenomena of increasing modulus with increasing temperature for a stretched elastomer. The thermoelastic effect, however, must also manifest itself in temperature changes being associated with pressure changes, particularly when the pressure changes (either positive or negative) are rapid such that adiabatic conditions are approximated. In these situations the temperature changes are maximum and occur without the transfer of heat, instantaneously and uniformly. Common situations that involve such pressure changes include injection molding, extrusion, cold forming, and shock wave transport through polymeric materials.

The magnitude of the temperature change as a result of small pressure changes under adiabatic conditions are predicted by the Thomson equation $(\partial T/\partial P)_Q = \alpha T/\rho c_p$, where α is the volume thermal expansion coefficient, c_p the specific heat, and ρ the density.[3–6] For materials such as many ceramics and metals,[7–9] the above equation can be used quite approximately to predict temperature changes from relatively high pressure changes because the parameters α, ρ, and c_p are not strongly pressure dependent for these materials. Furthermore, the only basic restriction on the derivation of the above equation is that of reversibility; i.e., the system must deform elastically and not plastically. This requirement is easily approximated by most metals and ceramics in intermediate pressure ranges, e.g., 300–400 MN/m^2. On the other hand, when applied to polymers, although the expression would trivially be expected to apply for small pressure changes, it would however be severely limited in being able to predict temperature changes resulting from large pressure changes. This is a result of the parameters α, ρ, and c_p being much more pressure sensitive for polymers than metals or ceramics. Further, the basic criteria of reversibility for polymers at intermediate pressures might be questioned particularly for glassy polymers below T_g because of the basic nonequilibrium nature of the glassy state of the polymers. Polymers in processing situations are not uncommonly subjected to rapid pressure changes of the order of 100–200 Mn/m^2, and an estimate of temperature changes in plastics is many times greater than those in metals,[6–8] e.g., 10–20 °C. Thus we investigated the temperature changes as a result of large pressure changes to primarly get an idea of the magnitudes involved and to a first approximation test the Thomson equation. In order to do these experiments at high pressures, it is required that the pressures be applied hydrostatically to minimize plastic deformation.

Thermoelastic studies to date have been performed primarily under uniaxial tension or compression, limiting the loads to small values because of the reversibility requirement. Binder and Müller[10] reported qualitative results of thermal measurements on poly(vinyl chloride) under uniaxial compression. Müller and Engelter[11,12] calorimetrically measured heats associated with elongation of some metals and polymers. They observed variations in the heats evolved during elastic, viscoelastic, and plastic deformation. Haward and Trainor[13] were the first to report a quantitative study of the thermoelastic effect in poly(methyl methacrylate) (PMMA) under both tensile and compressive stress. The stress range used was small and varied between 2 and 42 MN/m^2 over a temperature range of 295–355 °K. Their results showed that PMMA basically follows the Thomson equation over the stress and temperature range studied, except for small deviations at the lowest stresses which were attributable to experimental error. Gilmour, Trainor, and Haward[14] repeated these measurements on PMMA over a wider temperature range of 220–350 °K using improved instrumentation. They further extended the measurements to include polystyrene, polycarbonate, and some epoxy resins using uniaxial compressive stresses from 5 to between 25 and 50 MN/m^2. They concluded that the materials investigated all obey the Thomson equation suggesting that in general its application to polymers is valid in their measurements.

In general, all these studies were performed under rapid uniaxial extensions or compressions. However, they are limited to small stresses because of the limitations of plastic deformation and ease of failure of the glassy samples. Low stresses, however, produce only small temperature changes.

[a] CONICIT fellow.

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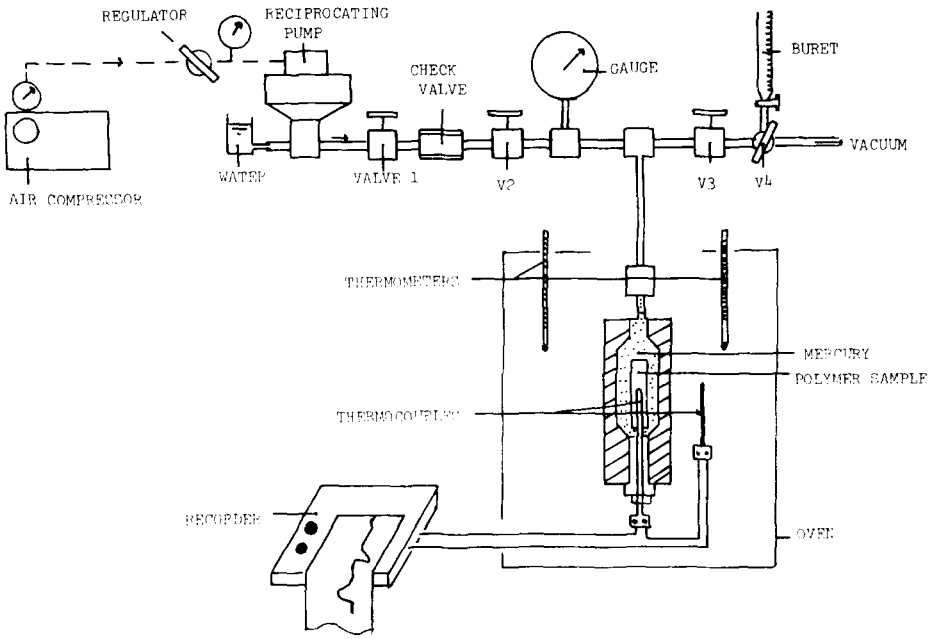


FIG. 1. Block diagram of high pressure system.

This work reports the results of an investigation of the thermoelastic effect in PMMA using hydrostatic pressure from 13 to 20 MN/m^2 and over a temperature range of 298–368 °K. The temperature changes over this range of pressures and temperatures were reversible as determined by equal temperature changes for identical pressure increases and decreases.

EXPERIMENTAL

Figure 1 illustrates schematically the experimental setup including the high pressure pump and equipment. A 1-hp standard air compressor with a regulated output variable to 100 psi is used to drive the air driven high pressure reciprocating pump (Teledyne Sprague). This pump also attenuates the pressure by a factor of 300 to a maximum of 30 000 psi (200 MN/m^2). The desired pressure was selected by a regulator located between the compressor and high pressure pump. The pressure was measured with two Bourdon gauges, each with a maximum of 50 000 psi and sensitivity of 500 psi/division. One junction of an iron-constantan thermocouple inside a 0.062-in.-diam. stainless steel sheath, the sample and mercury were located inside the high pressure cell, as illustrated in Fig. 2. With this arrangement the high pressure unit can easily be removed and reconnected to the high pressure line. Water is used as the pressure transmitting fluid throughout the system with the exception of the high pressure cell. The oven temperature was controlled to better than $\pm$ 0.5 °C. The second junction of the ΔT measuring thermocouple was located outside the high pressure unit but was located in direct thermal contact with it. This arrangement allowed us to measure directly only the temperature difference generated by the pressure variations and with maximum sensitivity since, when both junctions were at atmospheric pressure, the output of the thermocouple was virtually zero. The sample junction was located along the axis of the cylindrical shaped samples inside the high pressure cell. The sensitivity of the ΔT measuring system with the recorder on the 1-mV scale was about $\pm$ 0.1 °C.

The samples finally used were in the shape of cylindri-

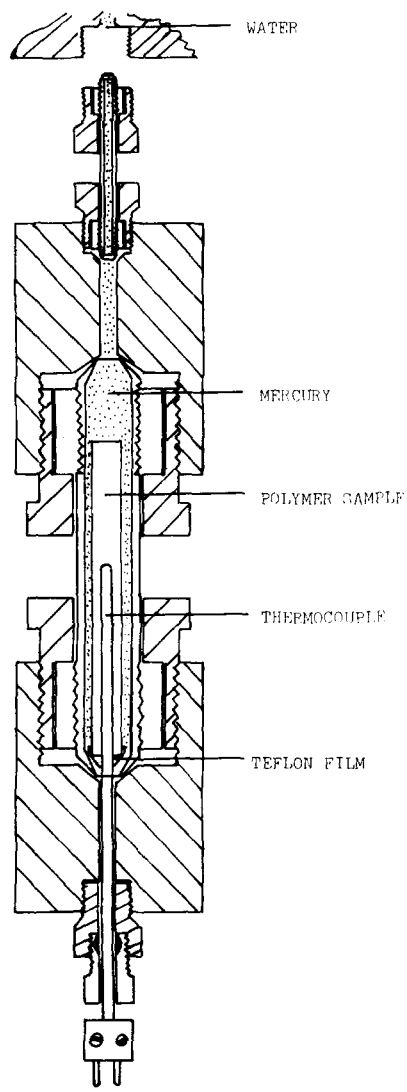


FIG. 2. Cross section of high pressure unit.

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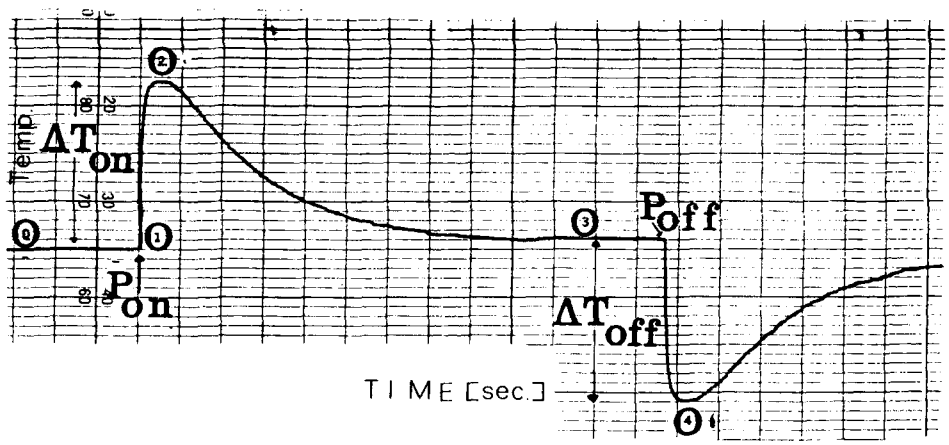


FIG. 3. Typical recording of thermoelastic effect corresponding to a delayed release of pressure.

cal rods 0.25 in. o.d. and 3.63 in. long. Because of problems encountered in attempting to form samples of this shape, we finally used commerically available rods purchased from Cadillac Plastic Inc., Detroit, Michigan. The material had a Tg of 105 °C as determined with a Perkin Elmer DSC-II, was transparent, and through ir analysis was confirmed to be pure PMMA. The molecular weight and distribution were not determined.

EXPERIMENTAL METHOD

A specific pressure was built up behind valve 2 (see Fig. 1). Rapid opening of valve 2 caused pressure to be transmitted almost instantaneously (a "pressure jet") to the polymer sample. The pressure was released by rapid opening of valve 3 to atmospheric pressure. Figure 3 shows a typical recording of the thermoelastic effect. In the figure we observe the following steps: from (0) to (1) represents the initial state; the atmospheric pressure is P_0; and the temperature T is the reference temperature or temperature of the oven. At (1) a pressure is applied, P_{on}. From (1) to (2) the polymer sample warms up. The temperature change ΔT_{on} is recorded. From (2) to (3) the sample relaxes until it reaches approximately the initial temperature T. At (3) pressure is rapidly released. From (3) to (4) the sample cools down by a ΔT_{off} amount. From (4) to (5), the polymer sample returns to the original conditions P_0 and T. A complete reversibility ($\Delta T_{on} = \Delta T_{off}$) was observed throughout the experiment.

RESULTS

Figure 4 illustrates the average adiabatic temperature increases measured at various temperatures and for various size pressure increments. All pressures were applied at atmospheric pressure, i.e., in every case $\Delta P = P - P_0$, $P_0 = 1$ atmosphere. The data is presented only for positive ΔP's and thus positive temperature increases since the magnitude of the temperature decreases upon removal of pressure for the same pressure increments is identical. Figure 5 illustrates the dependence of the ratio $\Delta T/\Delta P$ at various initial temperatures and as a function of pressure increment. It is surprising that these ratios all reach a constant value at high pressures, but this asymptotic value increases at increasing temperatures. This data is found to best fit an equation of the form $\Delta T/\Delta P = a - b\Delta P + c\Delta P^2$, where a, b, and c are empirical constants that vary with temperature. The values for these constants are summarized in Table I. Figure 6 illustrates the dependence of ΔT with ambient temperature at various constant pressure increments. This curve was included to illustrate the dramatic variation of the data at the highest temperatures, a behavior we feel is associated with the onset of the glass transition. These results can be empirically fitted to an equation of the form $\Delta T = d - eT - fT^2$, where d, e, and f are empirically determined coefficients that depend on pressure. Table II summarizes the calculated values of d, e, and f.

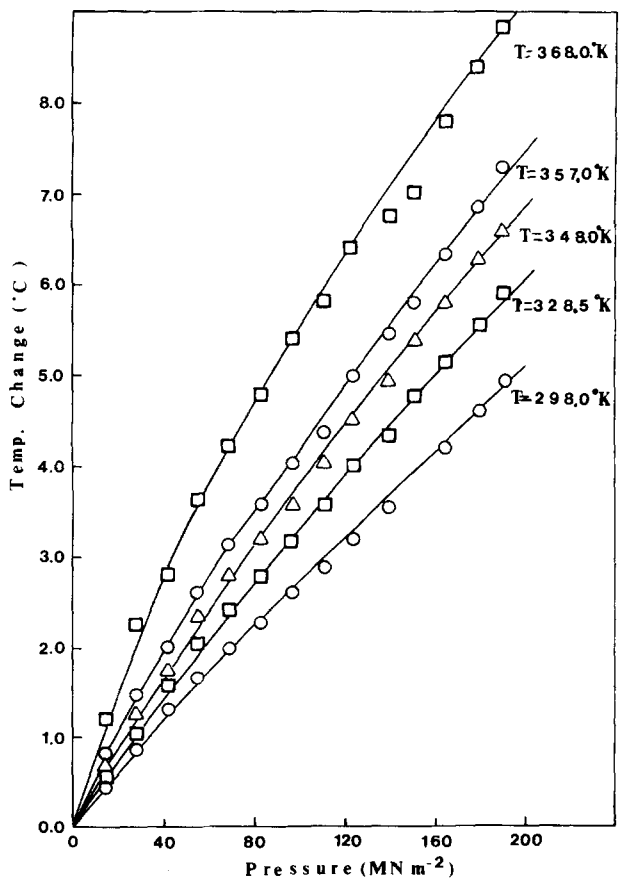


FIG. 4. Thermoelastic temperature change as a function of pressure for poly(methyl methacrylate).

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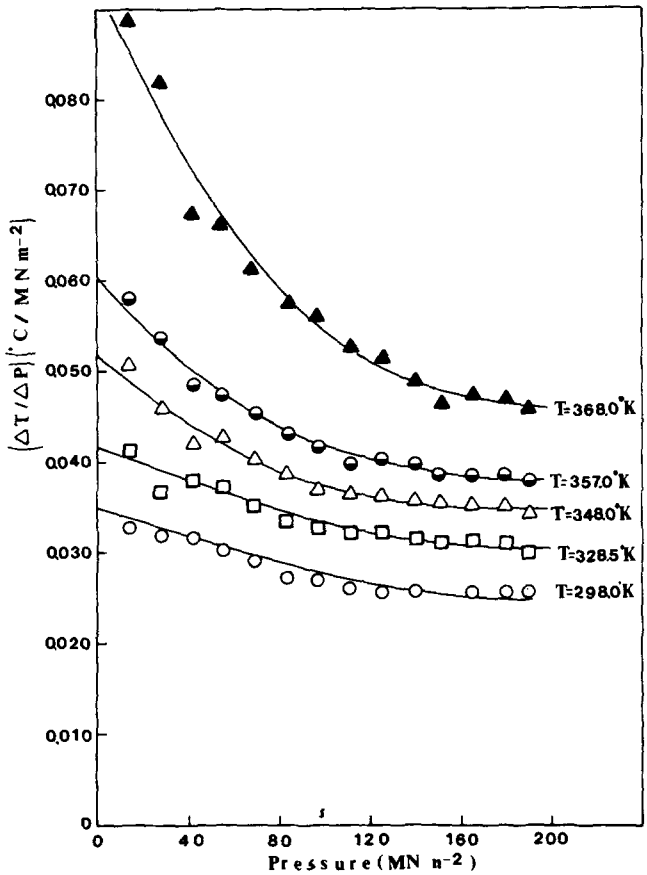


FIG. 5. Coefficient $(\Delta T/\Delta P)$ calculated as a function of pressure for poly-(methyl methacrylate).

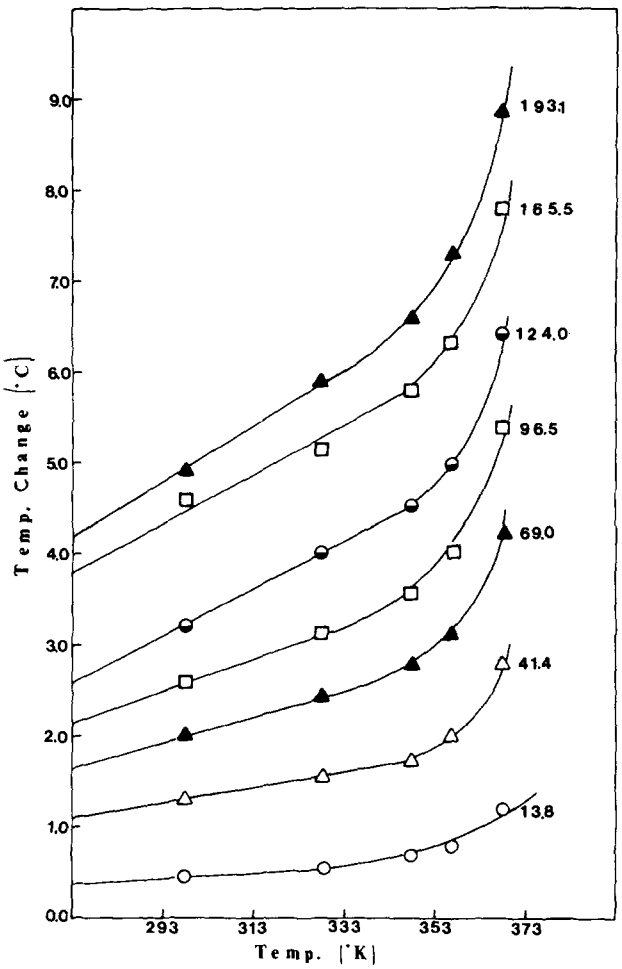


FIG. 6. Thermoelastic temperature change as a function of ambient temperature. The numbers indicate the pressure in MN/m^2.

DISCUSSION

The first point of concern is that of reversibility of the measurements, especially at the higher pressures which are required for these measurements to be thermoelastic. In all cases the data was perfectly reversible; that is, for the same magnitude pressure change, whether positive or negative, the absolute value of the temperature changes was identical. This is important since it implies that hydrostatic compression to these pressure values is reversible and can be legitimately treated thermodynamically. This is in contrast to uniaxial tension and compression stresses which are limited by plastic deformation to low values.

The second point concerns the actual magnitudes of the temperature increases. As illustrated in Fig. 4, at a pressure increment of 200 Mn/m^2, a thermoelastic temperature change of about 9 °C occurs just below the T_g. This increase is more than an order of magnitude greater than for common metals. Also relevant and as illustrated in Fig. 6, the $\Delta T/\Delta P$ increases dramatically around 370 °C, a behavior probably associated with the onset of the glass transition. If this behavior is real, then at standard processing temperatures around 200 °C, a thermoelastic temperature of 50–60 °C could be associated with pressure changes of 200 Mn/m^2. Such changes are by no means negligible.

Finally this work attempted to test to a first approxima-

TABLE I. Values for the constants a, b, and c in the equation $\Delta T/\Delta P = a - bP + cP^2$ for PMMA.

Temperature °K	$a\times10^2$ °C/MNm^{-2}	$b\times10^4$ °C/MNm$^{-2})^2$	$c\times10^7$ °C/MNm$^{-2})^3$	R^{2a}
298.0	3.480	1.12	3.34	0.973
328.5	4.175	1.18	3.12	0.939
348.0	5.175	2.08	6.30	0.963
357.0	6.019	2.72	8.31	0.980
368.0	9.337	5.63	17.00	0.973

[a] R^2 is the coefficient of determination.

TABLE II. Values for the constants d, e, and f in the equation $\Delta T = d - eT_\epsilon + fT_\epsilon^2$ for PMMA.

Pressure MN/m^2	d °C	e °C/°K	$f\times10^4$ °C/(°K)^2	R^{2a}
13.789	22.4202	0.1412	2.2661	0.939
41.368	43.1471	0.2688	4.3126	0.931
68.947	57.1183	0.3574	5.7920	0.951
96.526	71.5188	0.4467	7.2000	0.947
124.105	66.2771	0.4161	6.9000	0.957
165.473	65.3082	0.4088	6.8464	0.968
193.052	77.9640	0.4847	8.1000	0.973

[a] R^2 is the coefficient of determination.

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tion the applicability of the Thomson equation not in its differential form but in its incremental form where the ΔP's may be quite large. One test of this is to rewrite the equation in its incremental form as $\Delta T/\Delta P = \alpha T/\rho c_p$ and plot $\Delta T/\Delta P$ for various values of ΔP. At a given temperature the deviation of this plot from a constant value would be a measure of the amount of error to be expected if this equation were used to predict ΔT's from large ΔP's with constant α, ρ, and c_p. Figure 5 illustrates dramatically that the greatest error is at lower pressure increments and at higher temperatures. Further at higher ΔP's the ratio does in fact seem to be asymptotically approaching a constant value.

This decrease we feel is most strongly affected by the density which varies with pressure in a manner very similar to $\Delta T/\Delta P$.[15,16]

We are currently in the process of evaluating our data based upon numerous equations of state appearing in the literature and various published P-V-T data.[17] Initial attempts were unsuccessful not only in regard to giving correct predictions but also in regard to giving the correct theoretical dependencies as given by our empirical expressions. In this article we were primarily interested with the experimental aspects of this research and subsequent papers will follow concerning other systems as well as theoretical analysis of the data.

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