Fig. 2. Block diagram of the electronic circuit used in the pulse superposition method.

ent components. The only special equipment is the pulsed oscillator, which is a modified version of an Arenberg PG-650C oscillator. After modification, this generator can now produce rectangular-shaped, rf-modulated pulses of a duration up to 3 μsec at a maximum triggering rate of 200 kc/sec.[11]

The single crystals used for these velocity determinations were grown from saturated solutions of ammonium chloride; the details of the process have been described previously.[6] When the crystals had two flat and smooth natural faces no special preparation was needed for measurements in the [100] direction. Otherwise, two faces were cut perpendicular to the desired direction of propagation, and these faces were polished to optical quality. Four crystals were used: Crystals A, B, and C for measurements in the [100] direction, and crystal D for measurements in the [110] direction. The lengths (L) as measured with a light-wave micrometer at 23°C were (A) 1.8300±0.0001 cm; (B) 1.6453±0.0001 cm; (C) 0.9239±0.0001 cm, and (D) 1.2056±0.0001 cm. After almost every run the seal had to be changed, otherwise the quality of the echoes deteriorated. As a result of these changes the faces were slowly damaged and the path lengths were slightly decreased. Periodic length measurements were made and correction factors were applied.

A density of 1.52637 g cm^{-3} at 296°K was calculated from a lattice constant of 3.8750 Å, which is based on x-ray measurements around room temperature.[12] The path length ratio at 1 atm $L(T)/L(296°K)$ was calcu-lated from the thermal expansion data compiled by Sakamoto[13] and from the low-temperature x-ray data of Vegard and Hillsund.[14] Smooth-curve values of this ratio are given in Table I.

For measurements as a function of pressure at constant temperature, it is convenient[15] to introduce another path-length ratio $s=L_1/L_p$, where L_1 is the sample length at a given temperature and 1 atm and L_p is the length at the same temperature under an external applied pressure p. The calculation of $s(p)$ requires a knowledge of the isothermal compressibility as a function of pressure. At low pressures (i.e., in the disordered phase away from the lambda line) our present adiabatic measurements can be used to obtain an excellent approximation to $s(p)$. However, the difference between the isothermal and adiabatic compressibilities becomes very large in the transition region,[16] and it is necessary to make use of isothermal data for obtaining $s(p)$ values above the critical pressure. Bridgman[17] has directly measured the pressure dependence at 273° and 303°K of the length of a polycrystalline pressed rod of ammonium chloride. Comparison between Bridgman's data and ours at low pressures indicates that his values of $s(p)$ are systematically high by about 10% over a wide range of pressure. Thus, we have chosen $s(p)$ values at 273° and 303°K by correcting Bridgman's values with a constant multiplicative factor: $s-1=0.9(s_B-1)$. Values of $s(p)$ at other temperatures were chosen by extrapolating our low pressure

[11] This modification of the Arenberg pulsed oscillator (PG–650C–mod. 5–2) can now be obtained commercially from Arenberg Ultrasonic Laboratory, 94 Green Street, Jamaica Plains, Massachusetts.

[12] R. W. G. Wycoff, *Crystals Structures* (Interscience Publishers, Inc., New York, 1964), Vol. 1, Chap. III.

[13] Y. Sakamoto, J. Sci. Hiroshima Univ. **A18,** 95 (1954).

[14] L. Vegard and S. Hillesund, Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat. Naturv. Kl. No. 8 (1942); see Chem. Abs. **38,** 4488⁸ (1944).

[15] R. K. Cook, J. Acoust. Soc. Am. **29,** 445 (1957).

[16] L. Tisza, Ann. Phys. (N.Y.) **13,** 1 (1961).

[17] P. W. Bridgman, Phys. Rev. **38,** 182 (1931).

values in a manner consistent with the corrected Bridg-man curves. A plot of the $s(p)$ values adopted at various temperatures is shown in Fig. 3. Note that s varies by less than 2% over the pressure range involved in these experiments; thus a relative error of 5% in the extrapolation procedure will affect the value of s (and therefore the elastic constants) by only 0.1%.

Hydraulic pressure equipment of a conventional de-sign was obtained from the Harwood Engineering Com-pany, Walpole, Massachusetts. Pressures in excess of 12 kbar could be generated in the high-pressure cell, which was filled with a mixture of one-part Univis P38 oil and three-parts pure gasoline. The pressure values were determined from changes in the resistance of a calibrated manganin coil, which forms one arm of an equal-ratio dc Wheatstone bridge. Pressures could be measured with an accuracy of ±3 bar and could be maintained constant to within ±3 bar over a period of 60 min. The high-pressure cell was immersed in a regulated temperature bath, which could be kept con-stant to within $\pm0.05°$C at any temperature between $-30°$ and $+50°$C.

Measurements at 1 atm were made in a regulated temperature bath similar to that described by Lawson.[18] In essence, this consisted of a glass Dewar filled with methyl cellosolve, which could be cooled by circulating cold methanol through a copper coil. The temperature could be controlled to within $\pm0.05°$K at any value within the range from 215° to 320°K. Below 215°K, cooling was achieved with cold nitrogen gas by using an apparatus described previously.[6] Sample tempera-tures were measured with a copper–constantan thermo-couple.

For the measurements made at 1 atm, a variety of seal materials were used to cement the quartz trans-ducer to the sample crystal. Dow resin 276-V9 seals were used between 242° and 320°K since McSkimin[8,19] has determined the acoustical impedances and their temperature dependences for this material. Unfortu-nately, such seals break at the critical temperature on cooling. Measurements can be made down to about 195°K by using Apiezon N as a seal. Comparison between data obtained above the transition tempera-ture using Apiezon and Dow resin seals allows one to determine the phase-shift correction for these Apiezon seals. Nonaq stopcock grease was used to obtain data below 200°K, but it did not make as good a seal. Since the phase-shift correction term $\gamma/360f$ in Eq. (5) was always less than 0.02% at room temperature, it was possible to neglect the temperature dependence of γ without causing a serious error in the values calculated for the elastic constants at low temperatures.

For the measurements made at high pressures, it was necessary to use a seal which was insoluble in the hydraulic fluid. A suitable sealing material was found
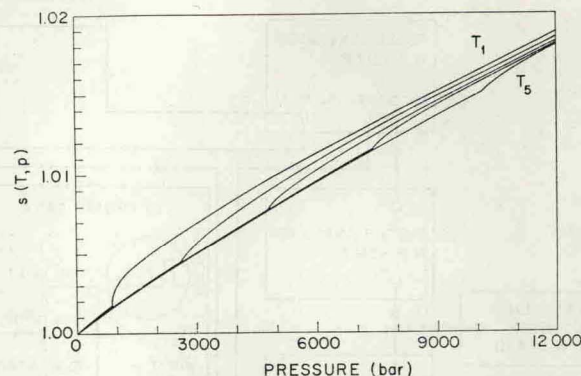
[18] A. W. Lawson, Phys. Rev. **57**, 417 (1940).
[19] H. J. McSkimin, IRE (Inst. Radio Eng.) Trans. Ultrasonics Eng., PGUE-5, 25 (1957).

FIG. 3. Path length ratio s as a function of pressure for tempera-tures $T_1 = 250.72°$K; $T_2 = 265.00°$K; $T_3 = 280.05°$K; $T_4 = 295.02°$K; $T_5 = 308.04°$K.

to be a polymer made by heating an equimolar mixture of phthalic anhydride and glycerine and then removing the water by vacuum distillation. All measurements were carried out at a rf frequency equal to the resonance frequency of a transducer at 1 atm. Thus, the phase angle γ will vary with pressure for two reasons: (a) the acoustical characteristics of the seal material vary and (b) the resonance frequency of the transducer varies. The effect of pressure on the seal is not known and has been neglected; the effect of pressure on the behavior of quartz transducers is known[9] and has been used to calculate γ as a function of pressure.

RESULTS

Constant-Pressure Data

Experimental data points are shown in Figs. 4, 5, and 6 for the elastic constants c_{11}, c_{44}, and C' as func-tions of temperature at 1 atm. Each of these points was obtained directly from a single measurement of the propagation velocity of sound waves modulated at 20 Mc/sec; see Eqs. (1)–(3). Measurements were also performed at 60 Mc/sec in the temperature range $220° < T < 300°$K, and those values agree with these 20 Mc/sec values within the limits of error. This ab-sence of dispersion is in agreement with previous meas-urements[6] between 5 and 55 Mc/sec.

Because of the strong attenuation of longitudinal waves in the vicinity of the critical point, it was not possible to use the pulse-superposition method to meas-ure c_{11} between 237° and 244°K. Instead, the variation of c_{11} in this temperature range was based on data obtained previously with a pulse-echo method.[6] Those older data now appear to have been subject to a system-atic error and require correction. They have been cor-rected by adding a constant (temperature independent) value of 0.120×10^{11} dyn cm^{-2} to all the previous data points; this yields agreement with our present data below 237° and above 244°K.

Shear waves were not attenuated strongly at any temperature inside the investigated range; however,