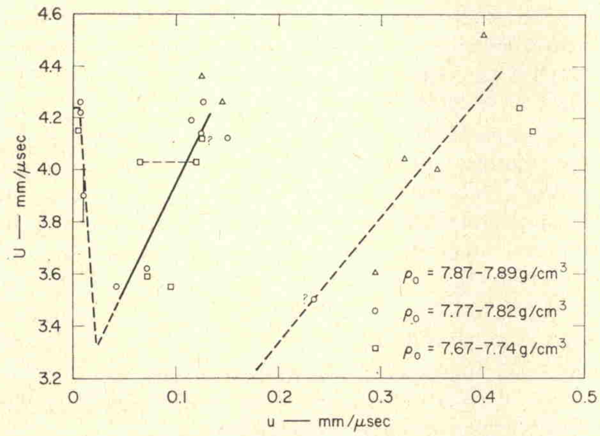

FIG. 9. Shock velocity vs particle velocity for 95/5 PZT (Curves are drawn for medium density).

rate value of first-wave amplitude was not obtained on this shot, but a value between 25 and 30 kbar is indicated.

PZT

The investigation of 95/5 PZT was hampered by the variation of density among the specimens. The Hugoniot data are presented in Table III and Figs. 9 and 10. The plotted points are grouped into three density ranges; the curves are drawn roughly for the intermediate range.

The results are rather incomplete but can be summarized as follows: Between about 40 and 140 kbar, a two-wave structure exists; the first-wave velocity equals c_L (including the density dependence) within experimental error. First-wave amplitude increases somewhat with initial density (see Table IV). One shot on low-density material indicated rapid attenuation of first-wave amplitude with propagation distance (in the presence of a second wave).

At lower stresses, the velocity decreased until, at $\sim$2 kbar, it returned to $\sim c_L$, i.e., there appears to be a cusp in the Hugoniot at $\sim$2 kbar.

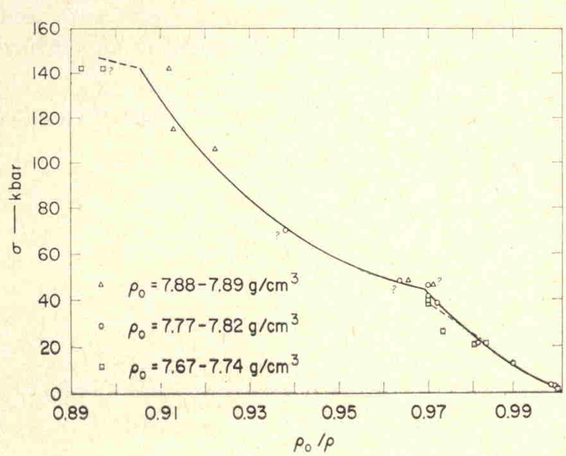

FIG. 10. Shock pressure vs compression for 95/5 PZT.

DISCUSSION

As has been discussed regarding pure BT by Reynolds and Seay,[2] there is little doubt that the $\sim$30-kbar cusp in the BT Hugoniot is the dynamic elastic limit. This is probably true in spite of the lack of the usual evidence of a nearly linear Hugoniot below the cusp and a velocity closely approximating the infinitesimal longitudinal sound speed (c_L). The other alternative is to identify the cusp as due to the Curie transition. Static data indicate that a hydrostatic pressure of about 19 kbar is sufficient to depress the Curie point to 20°C.[10] The short duration of the shock experiment might require a larger driving stress for the transition compared with that required for a quasistatic experiment. However, the apparent volume change at the cusp is some 20 times greater than the 0.1% associated with the Curie transition. Also, static uniaxial compression data (see Fig. 2) suggest that failure should occur under the uniaxial conditions of shock compression somewhere above 12 kbar; yet no other cusp is observed.

TABLE IV. Data on cusp at $\sim$40 kbar in Hugoniot for 95/5 PZT.

Shot No.	Initial density (g/cm^3)	Velocity (mm/μsec)	Stress (kbar)	Specimen thickness (mm)	Driving wave (kbar)
8881	7.67	(4.03)	38–21	5.6 max	70
8882	7.74	4.12	(39)	6.6 max	70
8881	7.81	4.19	38	6.6	70
8413	7.81	4.14	41	12.5	70
8445	7.82	4.26[a]	41	6.7	120
8703	7.89	4.36	43	5.1	115
8705	7.89	4.26	48	6.5 max	120

[a] This is not U_1 because initial state is $\sim$5 kbar, not 0. Estimated corresponding $U_1 \sim 4.10$ mm/μsec.

When a specimen was preheated to the cubic paraelectric phase prior to shocking, a nearly linear Hugoniot was obtained over the 13–30 kbar range covered, and the wave velocity corresponded closely with c_L^{cubic}. Thus the variation of wave velocity with amplitude for initially tetragonal material, from $\sim$5.5 (c_L^{tet}) at $<$1 kbar to $\sim$5.2 mm/μsec ($<c_L^{\text{tet}}$) at 5 kbar to $\sim$6.27 mm/μsec ($\sim c_L^{\text{cubic}}$) at 30 kbar, is associated with the ferroelectric nature of the material.

The subsonic velocity at 5 kbar may be due to strain relief by domain reorientation. Such an effect would not be expected in material of crystal density subjected to the uniaxial strain of the shock front. However, in porous material as used in this study, the strain is uniaxial only on a macroscopic scale, and domain reorientation to relieve strain at relatively low stress is quite possible.

The increase in wave velocity above c_L^{tet} beginning at 7 kbar was originally interpreted as indicating the onset of the Curie transition. The data in the vicinity

[10] G. A. Samara, Phys. Rev. 151, 378 (1966).

of 30 kbar, from both the room temperature and elevated temperature shots, are consistent with the material being in the high-temperature phase in each case. Furthermore, electrical measurements by Binder[4] showed that charge release was complete by ~7 kbar and suggested that the dielectric constant was abnormally high in this region.

Recently, Linde[11] found in careful recovery experiments that depoling was not complete in specimens shocked to well above 7 kbar (23 kbar in one case). Thus, it seems most likely that the onset of transition is near 7 kbar and that it is not complete until shock amplitudes reach the vicinity of the Hugoniot elastic limit.

For 95/5 PZT, the effect on the relative compression, ρ_0/ρ, of varying the initial density, ρ_0, is greatest for the highest pressure (140 kbar) shots. The specific volume at this pressure, however, is insensitive to ρ_0, probably indicating collapse of the porous structure. We must conclude, as for BT, that the first-wave amplitude of 30–50 kbar is a measure of the Hugoniot elastic limit. The effective volume change is less than expected for the porosities of 3% to 5% indicated by density measurements, but the actual porosity is probably less than this due to impurities. The first-wave velocities correlate nicely with measured sound speeds (which correlate with ρ_0; see Table IV).

Consideration of the Curie transition can probably be omitted as the cause of the 40-kbar cusp because the Curie temperature is high (220°C) and the indicated volume change is much too great (one should expect $\Delta V \sim 0.1\%$). There are, however, two other transformations which 95/5 PZT can undergo which may be pertinent to interpretation of the low-pressure data. At 70°C, a transformation from one ferroelectric form to another takes place.[12] The longitudinal sound speed was measured[13] in the FE_2 phase and found to be 2.5%–4% higher than in the low-temperature phase. The difference is too small to justify any definite statement as to the phase the material is in at 40 kbar, although the FE_1 velocities agree best with U_1.

It is found that, under hydrostatic pressures of only a few kilobars, nominally PZT compositions (there may be small additions of other materials) close to an antiferroelectric–ferroelectric phase boundary transform from FE to AFE.[14] The critical pressure for 95/5 PZT with 1 wt% Nb_2O_5 is about 4 kbar.[4] The volume change for $PbZr_{0.96}Ti_{0.04}O_3$ is about 1%. Both figures are for poled material, however, and may be different for virgin material. In any event, one would expect to see this transformation in the experiments reported here if the volume change is sufficiently large. It is tempting to so identify the cusp at about 2 kbar, even though the indicated volume change is 0.1%–0.2%. This would mean that the material was in the AFE phase at 40 kbar, and therefore the agreement between U_1 and c_L would be coincidental. No data are available on the elastic properties of the AFE phase.

Halpin[15] has made some measurements of charge release and of wave amplitude in 95/5 PZT. He reported a cusp in the Hugoniot at ~5 kbar and stated that charge release was essentially complete at 10 kbar; fractions of total charge released at 4.9 and 3.8 kbar were 40% and 21%, respectively (for normally sintered material of $\rho_0 = 7.72$ g/cm³; hot pressed material, $\rho_0 = 7.99$ g/cm³, gave slightly different numbers). Again, these data suggest that, if a transition is beginning at a wave amplitude of 2 kbar (or 5 kbar, after Halpin), it is not complete until much higher amplitudes are reached.

Another interpretation of the low-pressure data is that suggested to explain the "softness" of BT below 7 kbar, viz., that some domain reorientation may be occurring.

The observation that the Hugoniot for 95/5 PZT has a cusp at about 2 kbar, while the Hugoniot for 52/48 PZT has one at such a low stress as to go unobserved by Reynolds and Seay, is consistent with the static stress–strain curves of Fig. 2, if the same mechanism is active in the static and dynamic experiments.

ACKNOWLEDGMENTS

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