Quasi-isentropic compression of liquid argon at pressures up to 600 kbar

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We have experimentally investigated the compressibility of liquid argon in a cylindrical copper casing at pressures up to 600 kbar. The amount of compression of the casing was measured by the gamma-graphic method; the pressure was determined from gas-dynamic calculations. We demonstrate good agreement between our experimental results and calculations. Our investigation of compressed argon revealed no anomalies connected with a transition to the metallic state up to densities of 4.2 gm/cm^3. Comparison with shock adiabatics demonstrates that the compression process under study was satisfactorily isentropic.

INTRODUCTION

Solid argon, which has a close-packed crystal structure, is of great interest in connection with investigations of phase transitions accompanied by metallization. Recently, a large amount of material has been accumulating on the behavior of condensed argon[1–4] under compression. In Ref. 4, the compressibility and temperature behind a shock wave in liquid argon were measured for pressures up to 700 kbar, and equations of state were derived for the solid and liquid phases. A detailed analysis of the experimental and theoretical data was carried out in the course of these investigations, in which the argon was made to condense under both static and dynamic conditions. An explanation was given for why the measured brightness temperature of argon lags behind the temperature calculated from an equation of state, using a theory which takes into account the kinetic processes which establish thermal equilibrium between electrons and the lattice. In Ref. 5, the electronic conductivity of Ar behind a shock front under pressures up to 640 kbar was measured up to $10^4(\Omega - \mathrm{m})^{-1}$. None of these studies of liquid argon, including the electronic conductivity measurements, show any clear anomalies under compression. However, a softening of the shock adiabatic is observed in the region of pressures above 300 kbar, which is related to the thermal excitation of electrons from valence to conduction band. It is possible to observe this same thermal electronic excitation effect, both experimentally and theoretically, in the results of Ref. 6 on the compression of ionic crystals, and also in those of Refs. 3, 4, 7 on shock compression of argon and xenon.

As was shown in Ref. 8, the conversion of a dielectric to a metal is a first-order phase transition terminating on a critical point only at low temperatures; at higher temperatures a continuous transition occurs. This latter situation is typical for compression of materials under shock loading: as the density and temperature increase, electrons from the valence band are excited into the conduction band, leading to an increase in the electrical conductivity of the material. The relaxation time of the phase transition can be longer than the traversal time of the shock wave through the material under study; as a result, a new phase may not be established under shock compression.

In comparison with shock loading, quasi-isentropic loading is a smoother and slower process. Therefore, its use leads to higher compressions and longer times over which the high pressure is applied, which relaxes the conditions for observing a phase transition. By using this method, the authors of Ref. 9 observed an anomaly in hydrogen which was interpreted as a phase transition to the metallic state in the pressure region ~ 3 Mbar.

In this article we measure the density of liquid argon compressed within a cylindrical shell via the gamma-graphic method in the pressure range 100 to 600 kbar. These investigations showed good isentropic compression, and up to 600 kbar no anomalies appeared which could be associated with a phase transition to the metallic state. The equation of state derived in Ref. 4 gives a good description of our experimental data. We confirm the conclusion arrived at in Ref. 4 that argon does not become metallic up to a density of 4 gm/cm^3. After we carried out these measurements, a paper written by American investigators[10] appeared on the isothermal compression of argon at $T = 298$ K up to a pressure of 800 kbar; their experimental data is in excellent agreement with the isotherms calculated using the solid-phase equation of state from Ref. 4.

EXPERIMENTAL RESULTS

The experiment reported here is analogous to the one described in Ref. 9. Under the action of the detonation products produced by exploring a cylindrical charge of explosive material, a copper shell with liquid argon in its interior cavity is accelerated radially inward. The motion of the shell was recorded with the help of a transmission gamma-graphic setup with small exposure time. An x-ray photograph illustrating the boundaries of the copper shell was processed using an IFO-451 microdensitometer. The photometry was carried out over 10 cross-sections of the central portion of the image. The final results of the measurement were obtained by averaging the values of the cavity radius over all photometric cross-sections of the x-ray photograph.

X-ray photographs of the shell cavity in its original state and at the instant of compression are shown in Fig. 1 for $\delta = \rho/1.77 \sim 1.5$ (ρ is the density of argon). The error in the values of the compressed-argon density measured in these experiments is determined largely by errors in the measured sizes of the compressed cavity, and in less than 6%. From the figure, a high degree of uniformity is apparent in the motion of the shell, with a clear absence of radial inhomogeneity in the density of the compressed argon. Gas-dynamic calculations show that at the moment of compression, i.e., at $\delta = 2.35$, the radial inhomogeneity of the argon is less than 7%, and was even smaller at lower compressions. From these calculations it follows that the length of time during

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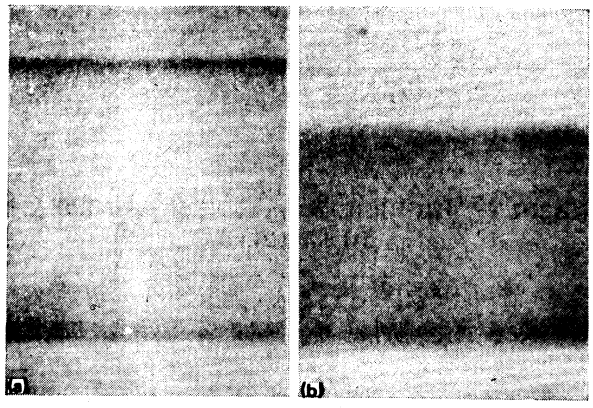

FIG. 1. X-ray photographs: a—in the original state; b—at the instant of compression.

which the argon is in its compressed state is several times longer than the time under shock compression.

In Fig. 2 we compare experimental and theoretical trajectories of the internal boundary of the shell. As a measure of error, we show the root mean square deviation of the average measured radius with a confidence level of 0.9. The good agreement between the calculated and experimental curves attests to the correctness of our calculation for the pressure within the compressed argon.

COMPARISON OF CALCULATED AND EXPERIMENTAL DATA

The values of the argon pressure and density in the cavity and the trajectories for motion of the internal boundary of the shell were determined from gas-dynamic calculations,

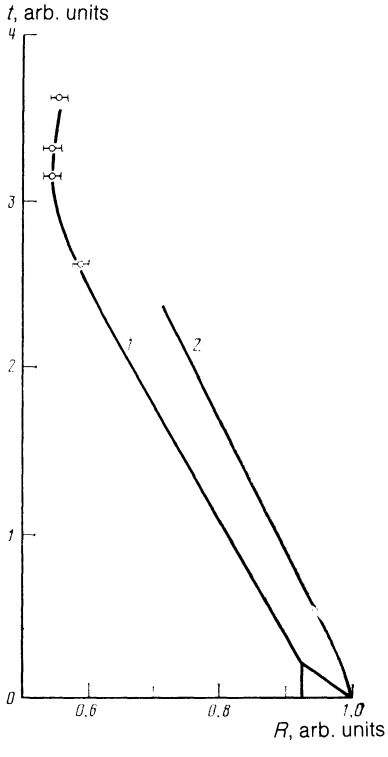

FIG. 2. R–t diagrams of the motion of the shell boundary: 1—the internal boundary; points are experiment, the continuous curve is theoretical; 2—external boundary (calculated).

using the BAL program[12] which employs equations of state for materials encountered in structures, and the equation of state of argon used in Ref. 4. It is clear from Fig. 2, that the calculated trajectory is in good agreement with experiment.

The calculated segments of the isentropes and the values of pressure and density at the argon-shell boundary are compared with experimental data in Fig. 3. In this figure we present data on the compression of argon by one and two shock waves, and the $T = 298$ K isotherm from Ref. 10. Good agreement is apparent between the isotherm calculated using the equation of state from Ref. 4 and the experimental isotherm in the range up to 800 kbar. In addition, this analysis shows good agreement between the isotherms calculated from the Ref. 4 equation of state and those from Ref. 10 up to 7 Mbar.

For isentropic compression (see Fig. 3), the calculated and experimental results agree very well with each other, and for the same pressure they lie in a region of densities significantly larger than those densities attainable by double shocks, let alone single shocks; the experimental points all lie near the "cold" curve P_x.

Let us estimate the entropy which corresponds to the conditions of our experiment; we will show how isentropic the experiment is, and also compare the temperatures corresponding to single-shock, double-shock and isentropic compression.

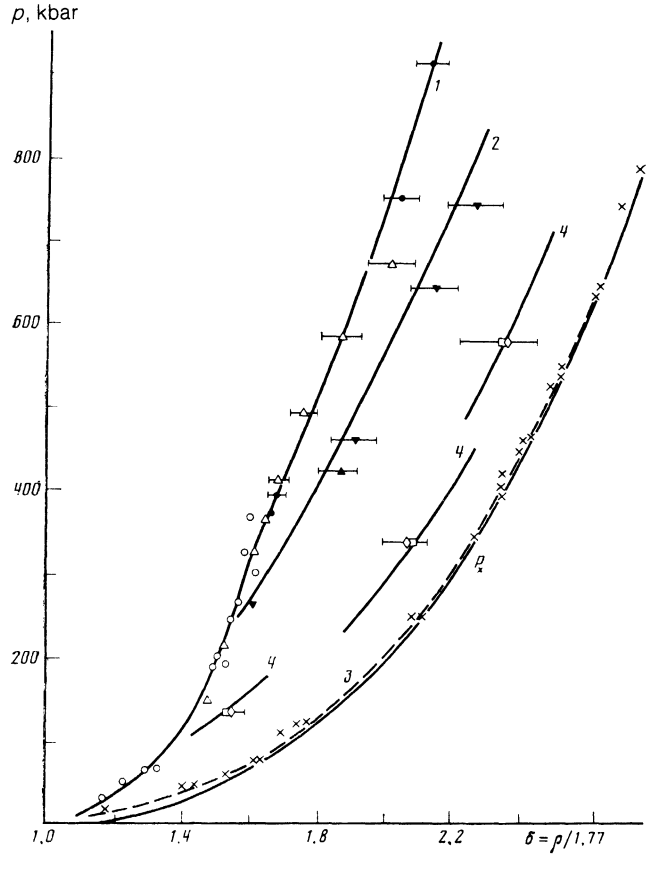

FIG. 3. Compression of liquid argon. Experiment: single-shock compression is ○ (Ref. 1); ● (Ref. 3); △ (Ref. 4); double-shock is ▼ (Ref. 2); ▲ (Ref. 4); isothermal compression is × (Ref. 10); isentropic compression is ◇ (Ref. 10). Calculations: curves 1, 2 and P_x are from Ref. 4; 3 is an isotherm for $T = 298$ K; 4 is an isentrope from this paper. □ is from a gas-dynamics calculation at the shell-argon boundary.

TABLE I.

	$\delta=\rho/1.77$	$S_L/3R$	T_S, K	T_1, K	T_2, K
1	1.52	3.95	2900	6 100	–
2	2.07	3.22	2200	22 000	11 200
3	2.35	3.6	4000	29 000	15 000

The free energy in the liquid phase takes the form[4]

$$F_L=E_x+3RT\{\ln[(\Theta/T)(1+z)^{1/2}]-b\}+3RT_0 f, \quad (1)$$

from which we obtain the entropy

$$\frac{S_L}{3R}=b+1-\frac{\Theta}{T}-\frac{z}{2(1+z)}-\frac{1}{2}\ln(1+z), \quad (2)$$

where in Eqs. (1) and (2),

$$E_x=\frac{3}{\rho_K}\sum_{i=1}\frac{a_i}{i}(\delta^{i/3}-1), \quad (3)$$

and $\delta=\rho/\rho_k$, where ρ_k is the density at $P=0$ and $T=0$;

$$\Theta=\frac{\Theta_0}{C_x(\delta=1)}\delta^{1/3}\left(C_x^2-n\frac{2P_x}{3\rho}\right)^{1/2}, \quad (4)$$

here

$$C_x^2=dP_x/d\rho, \quad P_x=\rho^2\,dE_x/d\rho, \quad z=lRT\left(C_x^2-n\frac{2P_x}{3\rho}\right)^{-1},$$
$$f=C+\frac{a}{r}\left[\left(\frac{\delta}{\delta_0}\right)^r-1\right].$$

The parameters in these equations have the following values[4]

$\rho_k=1.77$ gm/cm^3, $n=2$,
$a_1=-1057.33$, $a_2=3467.23$, $a_3=-3837.22$, $a_4=1427.32$ (a_i, in kbars), $T_0=83.8$ K, $\Theta_0=93.3$ K,
$\delta_0=0.8$, $l=3$, $r=1$, $a=1.7925$,
$b=0.694$, $C=-0.0589$.

The values of entropy corresponding to the experimental data are shown in Table I, and the calculated isentropes are shown in Fig. 3. Also shown in the table are the values of temperature for the same density on the isentropes (T_s) and on the shock adiabats for single-shock (T_1) and double-shock (T_2) compression. As the comparison shows, the temperature on an isentrope for parameters corresponding to the experimental data are significantly smaller than the temperatures on the shock adiabats. Thus, e.g. at a density $\rho=3.66$ gm/cm^3 ($\delta=2.07$), the temperature for isentropic compression is five times lower than for double-shock compression, and ten times lower than for single-shock. The thermal components of the pressures equal 100, 400 and 600 kbars.

Investigation of isentropic compression of liquid argon in the pressure region up to 600 kbar has shown no apparent anomalies. This confirms the conclusion arrived at in Ref. 4 that argon does not enter the metallic state in the regions investigated here.

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