Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 53, No. 5, 1648–1651, 1 September 1970
Printed in U. S. A.

Shock Compression of Solid Argon*

R. D. DICK AND R. H. WARNES
Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544
AND
J. SKALYO, JR.†
Brookhaven National Laboratory, Upton, New York 11973
(Received 27 March 1970)

The Hugoniot of solid argon (initially at 75°K and approximately 1 bar) has been determined using standard shock-wave techniques. Sample pressures ranged 18–645 kbar with associated densities of 1.39–2.18 times the initial density of 1.65 g/cc. Utilizing an exp-6 interatomic potential, a computed fit was obtained which was in excellent agreement with the data up to 300 kbar. The deviation between theoretical and experimental Hugoniot above 300 kbar is interpreted as either due to melting or to an inadequate model and potential form.

I. INTRODUCTION

The rare gases are elements whose physical properties are most easily interpreted theoretically because they are inert and form molecular crystals. Some recent investigations have extended equation-of-state data for argon[1–3] and xenon[4] by shock compression methods to pressures and temperatures not readily reached in static measurements. As a result of the high compression, the repulsive part of the interatomic potential can be measured for widely varying interatomic separations. Also a density region can be reached where electronic redistribution affects the properties predicted by simple theories.

The shock compression measurements of van Thiel and Alder[2] on liquid argon (samples initially at 86°K, 2 bar and at 148°K, 70 bar) indicate the repulsive part of the potential is much softer than that of the Lennard-Jones and Devonshire (LJD) (6–12) potential.[5] The measurements also indicated that the relevant parameters describing a simple potential are slightly dependent on the density region explored. Similar shock compression measurements by Keeler *et al.*[4] on xenon indicate a Hugoniot similar to that of argon when analyzed on a corresponding states basis except at the very highest pressures (approx. 500 kbar in xenon), where a substantial departure is encountered.

This deviation has been explained by Ross and Alder,[6] and in more detail by Ross,[7] on the basis of differences in the behavior of the electronic band structure at the higher densities. At the highest pressures, the xenon Hugoniot indicates a change in the compressibility due both to an electron population of the conduction band at the high temperatures reached and to a narrowing band gap. The band gap is not expected to narrow in argon at the highest shock pressures (approx. 350 kbar) and the temperature reached is not sufficient to populate the conduction band.

Based on their liquid-argon measurements van Thiel and Alder[2] indicate that, in the pressure–volume plane, the Hugoniot crosses the liquidus curve into the mixed phase region at about 0.7 kbar and re-enters the liquid phase at 45 kbar. Further calculations indicate the possibility of tracing out the melting line by starting

TABLE I. Solid argon Hugoniot data.[a]

Shock velocity (km/sec)	Particle velocity (km/sec)	Pressure (kbar)	Volume (cc/mol)	2024 Aluminum shock velocity (km/sec)	V/V_0
2.00±0.01	0.56±0.08	19±3	17.41±0.99	5.84±0.06	
2.44±0.01	0.78±0.06	32±3	16.44±0.63	6.04±0.05	
2.68±0.02	0.94±0.08	42±3	15.71±0.68	6.19±0.06	
3.53±0.02	1.29±0.06	75±4	15.35±0.44	6.54±0.05	
4.17±0.02	1.78±0.06	122±4	13.90±0.36	7.03±0.06	
5.02±0.06	2.28±0.06	188±5	13.22±0.34	7.57±0.06	
5.31±0.01	2.35±0.02	206±2	13.48±0.10	7.67±0.02	
5.69±0.04	2.49±0.09	233±9	13.56±0.41	7.83±0.09	
6.13±0.07	3.02±0.03	305±4	12.30±0.22	8.38±0.03	
6.75±0.03	3.32±0.02	370±3	12.30±0.12	8.74±0.02	
7.21±0.03	3.60±0.05	428±6	12.13±0.19	9.05±0.05	
7.65±0.02	3.99±0.05	503±7	11.57±0.17	9.48±0.05	
8.49±0.07	4.60±0.06	645±9	11.09±0.22	10.17±0.05	

[a] Initial density is 1.65 g/cc at 75°K.

with argon at differing initial temperatures. In particular, the solid argon Hugoniot at 20°K is expected to cross the melting line between 160 and 330 kbar.[8]

In the present paper, measurements on the Hugoniot of solid argon (initially at 1 bar and 75°K) are reported. The higher initial density of the solid compared to the liquid has the advantage of permitting measurements to higher pressures. Also, by starting with the solid, the added complications produced by the Hugoniot crossing the melting line twice at low pressures would be avoided.[2] Additionally, the determination of a point on the melting curve could possibly be detected by a discontinuous change in slope in the shock velocity (U_s)–particle velocity (U_p) relation.

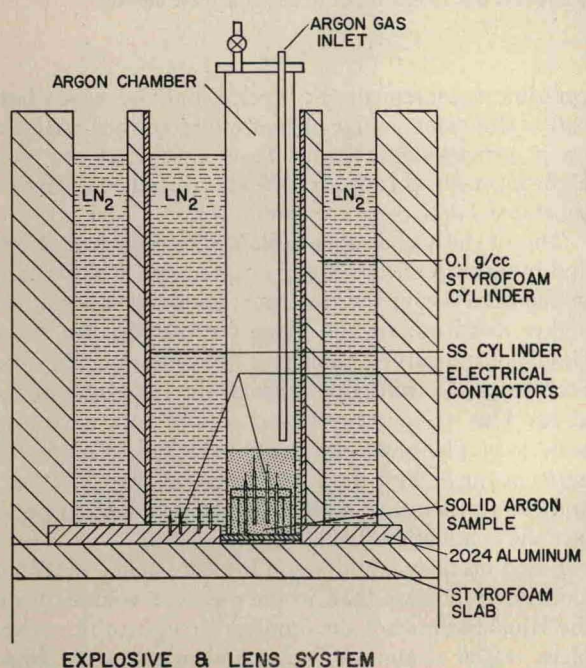

FIG. 1. Cross-sectional view of the apparatus used for the solid argon experiments.

II. EXPERIMENTAL APPARATUS

The experiments consisted of measuring the shock velocities in argon samples and in 2024 aluminum standards. The shock velocity was varied by appropriate choices of the explosive system, and was measured by the electrical pin-contactor technique. The experimental apparatus is shown in Fig. 1. The argon chamber is constructed alternatively from either a Pyrex glass tube or a stainless-steel cylinder closed at the sample end by a 2024 aluminum cover. After flushing with argon gas (99.99% pure), the solid sample is formed by slowly lowering the chamber into a liquid nitrogen bath. A visual inspection revealed the solid argon to be homogeneous, clear, and free of vapor snakes.

Since argon is nonconducting, coaxial electrical pin contactors[9] were placed in both the sample and the standard. The pin positions were measured at room temperature and corrections were made for thermal contraction to 75°K. For the solid argon, the pins were mounted in a disk supported above the 2024 aluminum cover. The solid was then allowed to grow around the pins in apparent intimate contact. In all cases, the distance between the lowest and highest pin levels was kept as small as possible (approx. 3 mm) in order to minimize the effects of attenuation on the pressure pulse. For this same reason, it was necessary to fit the argon sample holder into a recess in the 2024 aluminum plate. The insulating styrofoam slab shown in Fig. 1 was removed a few seconds before the explosive was detonated, allowing the aluminum plate to rest directly on the explosive.

III. RESULTS AND INTERATOMIC POTENTIAL

The Hugoniot data of the solid argon are presented in Table I. From measured shock velocities in the sample

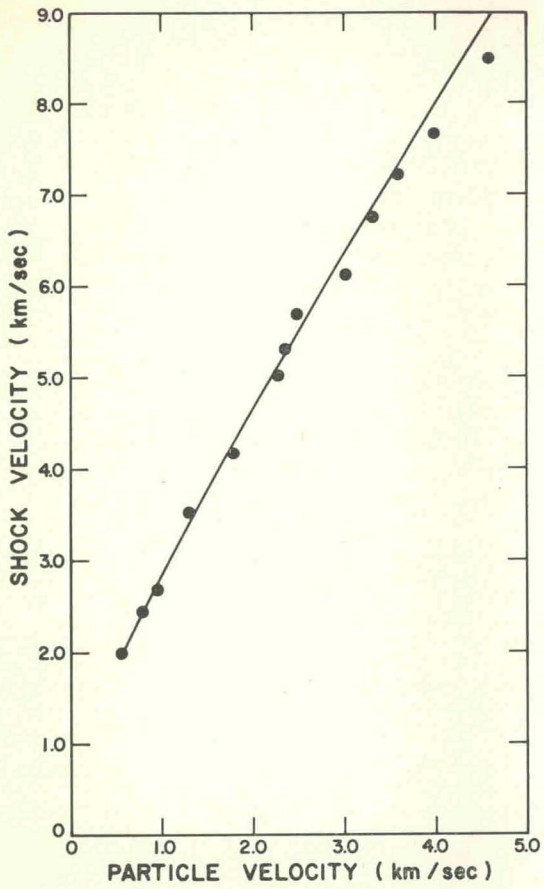

FIG. 2. Shock velocity versus particle velocity plot for solid argon showing the experimental Hugoniot data (solid circles) and the calculated Hugoniot curve (solid curve) from an exp-6 potential.

and in the 2024 aluminum standard, the pressure (P), volume (V), and particle velocity are determined from the impedance match method[10] and the Rankine–Hugoniot relations

$$P=\rho_0 U_s U_p, \qquad V=V_0(1-U_p/U_s), \quad \text{and} \quad V_0=1/\rho_0, \tag{1}$$

where ρ_0 is the initial density and U_s and U_p have been defined previously. It was necessary to adjust the 2024 aluminum Hugoniot[11] (measured at an initial temperature of 300°K) to the initial experimental temperature of 75°K. The U_s–U_p relation of the standard at this temperature is

$$U_s=5.387+1.335U_p. \tag{2}$$

A density of 2.820 g/cc at 75°K and a Gruneisen ratio of 2.0 for the standard were also utilized in the analysis. The errors given for the shock velocities are single standard deviations determined from a least-squares fit to the time–distance data. The least-squares fit is corrected also for a slight amount of tilt of the plane of the pressure wave with respect to the plane of the aluminum plate.

The U_s–U_p data of Table I are depicted in Fig. 2. The data can be interpreted as two straight line segments. A least-squares fit to the data in the interval $2.00\leq U_s\leq 5.79$ km/sec results in the equation

$$U_s=(1.04\pm0.11)+(1.79\pm0.06)U_p \tag{3}$$

and in the interval $5.79\leq U_s\leq 8.50$ km/sec,

$$U_s=(2.14\pm0.30)+(1.38\pm0.07)U_p. \tag{4}$$

The intersection occurs at $U_s=5.79$ km/sec and $U_p=2.65$ km/sec, which corresponds to a pressure of 253 kbar.

The above interpretation, however, is not unique. An equally good fit can be made for all shock velocities by

$$U_s=(0.87\pm0.12)+(2.08\pm0.11)U_p-(0.09\pm0.02)U_p^2. \tag{5}$$

It is noted that both interpretations result in an intercept ($U_p=0$) which agrees, within the errors, with the bulk sound speed (1.05 km/sec) calculated from adiabatic compressibility data.[12]

The Hugoniot of argon has been calculated for the exp-6, LJD (6–12), and the modified Morse potential. In the computation[13] the cell model of Lennard-Jones and Devonshire[14] was used and the pair potentials were assumed to be additive. The computation was performed utilizing a computer program developed by Fickett.[15]

The best fit to the experimental data occurred with the exp-6 form of the interatomic potential,

$$\Phi(r)=[kT_0/(\alpha-6)]\{6\exp[\alpha(1-r/r_0)]-(r/r_0)^{-6}\}, \tag{6}$$

where α is the family parameter representing the steepness of the repulsive part of the potential. The potential minimum is at r_0 with a potential well depth of kT_0. The relevant parameters were determined to be $T_0=118$°K, $r_0=3.70$ Å, and $\alpha=14.5$. These values are consistant with previous shock data,[2] molecular-beam data,[16] and various calculations.[13,17–19] The calculated U_s–U_p relation and the experimental data are illustrated in Fig. 2. They agree up to $U_s=6$ km/sec. The resultant Hugoniot is illustrated in Fig. 3 for comparison with the earlier liquid[2] and gas[3] studies.

IV. CONCLUSIONS

The Hugoniot of solid argon has been determined from 18 to 645 kbar, and the data have been fit with an exp-6 interatomic potential with good agreement up to 300 kbar. For this pressure range the assumption of pair additivity and the choice of the potential form is reasonable. The departure of the calculated Hugoniot from

the experimental data occurs at higher pressures and temperatures. Apparently, the cell model needs to be modified to account for phenomena such as populating the conduction band, narrowing the band gap, ionization, and liquefaction. Under these conditions the potential form may also require modification.

The U_s–U_p data can be interpreted two different ways. The two-line segment interpretation, Eqs. (3) and (4), implies a phase transformation at 253 kbar. Since solid argon has a close-packed crystal structure, a polymorphic phase change is not expected and the transformation would likely be melting. In the pressure–volume plane a melting curve[2] calculated by the Monte Carlo method intersects the solid argon Hugoniot at about 250 kbar, agreeing well with the pressure associated with the discontinuous slope change in the U_s–U_p relation. The temperature calculated from the exp-6 potential at the transition pressure is about 5900°K.

An alternate interpretation is that the data are represented by a single quadratic curve, Eq. (5). This would indicate that no transition occurs over the investigated pressure range. Some support for this interpretation arises from the slight curvature present in the theoretical U_s–U_p relation.

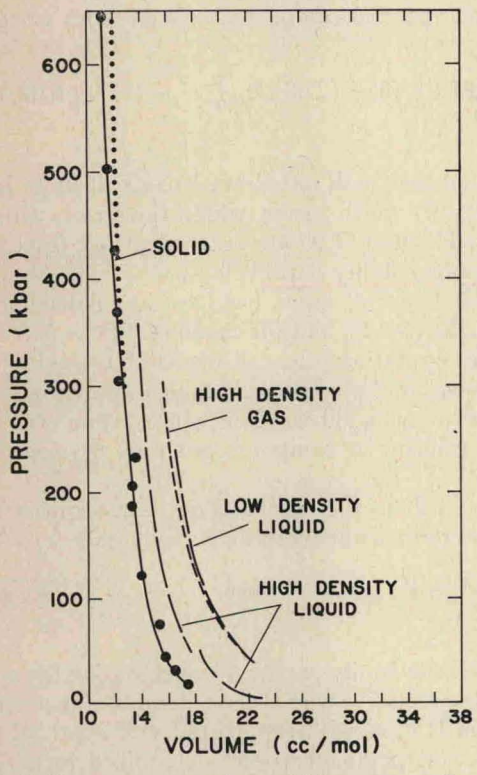

FIG. 3. Pressure versus volume plot for argon. —●—, experimental solid argon Hugoniot (V_0=24.21 cc/mol); – –, high- (V_0=28.43 cc/mol) and low- (V_0=43.46 cc/mol) density liquid argon Hugoniot data from Ref. 2; - - -, high- (V_0=40.93 cc/mol) density argon gas Hugoniot data from Ref. 3; •••, solid argon Hugoniot calculated from an exp-6 potential.

ACKNOWLEDGMENTS

We wish to thank C. D. Reese and T. E. Gould for their invaluable aid in carrying out the experimental program. We are indebted to Wildon Fickett and Stan Landeen for useful discussions throughout this investigation.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Experimental investigation started while employed at the Los Alamos Scientific Laboratory.

[1] J. Dapoigny, J. Kieffer, and B. Vodar, J. Phys. Radium **16**, 733 (1955).
[2] M. van Thiel and B. J. Alder, J. Chem. Phys. **44**, 1056 (1966).
[3] J. Wackerle (private communication).
[4] R. N. Keeler, M. van Thiel, and B. J. Alder, Physica **31**, 1437 (1965).
[5] M. Ross and B. J. Alder, J. Chem. Phys. **46**, 4203 (1967).
[6] M. Ross and B. J. Alder, J. Chem. Phys. **47**, 4129 (1967).
[7] M. Ross, Phys. Rev. **171**, 777 (1968).
[8] B. J. Alder and M. van Thiel, Phys. Letters **7**, 317 (1963).
[9] R. D. Dick and T. E. Gould, Rev. Sci. Instr. **36**, 143 (1965).
[10] M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, pp. 1–63.
[11] W. J. Carter, S. P. Marsh, J. M. Fritz, and R. G. McQueen, "The Equation of State of Selected Materials for High Pressure References," LASL Rept. LA-DC-9990, 1968.
[12] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957).
[13] W. Fickett and W. W. Wood, Phys. Fluids **3**, 204 (1960).
[14] L. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A163**, 53 (1937).
[15] W. Fickett, "Detonation Properties of Condensed Explosives Calculated with an Equation of State Based on Intermolecular Potentials," LASL Rept. LA-2712 (1962); "Intermolecular Functions for Some Molecules from Available Experimental Data," LASL Rept. LA-2665 (1962).
[16] S. O. Colgate, J. E. Jordan, I. Amdur, and E. A. Mason, J. Chem. Phys. **51**, 968 (1969).
[17] J. S. Brown, Proc. Phys. Soc. (London) **89**, 987 (1966).
[18] F. W. De Wette and R. M. J. Cotterill, Solid State Commun. **6**, 227 (1968).
[19] P. K. Salzman, A. F. Collings, and C. J. Pings, J. Chem. Phys. **50**, 935 (1969).