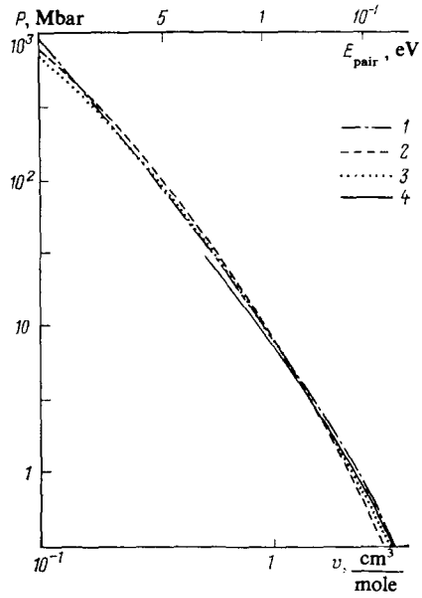

FIG. 2. The cold-compression curves of helium. Calculations: 1) QSM[2]; 2) empirical potential[3]; 3) theoretical potential[7]; 4) effective empirical potential.[6] E_{pair} is the interaction energy per pair of atoms.

for hexagonal close packing (the energy difference between different forms of close packing in the compression range studied is $< 1\%$). Empirical pair potentials, describing the repulsive part of the potential, were used.[3] Because of the short range of the repulsive forces most of the total pressure in the pressure range studied is created by the interaction with the atoms in the first coordination sphere (for He: $\sim 90\%$ at $P \sim 10$ Mbar and $\sim 80\%$ at $P \sim 100$ Mbar). In the calculations illustrated in the figures, summation extended only over the first coordination sphere. The cold-compression curve of He obtained in this manner (see Fig. 2) at pressures $P < 1$ Mbar is in agreement with the data extracted from shock-compression measurements, while in the range up to $P \sim 600$ Mbar the curve agrees with the asymptotic quantum-statistical model of matter. This provides a basis for regarding the truncation of the summation at the first coordination sphere as an efficient method for taking into account the nonadditive corrections for compressions up to pressures of several hundreds of Mbar.

The results of the calculations of the cold compressibility of molecular hydrogen presented in Fig. 1 were obtained using an effective spherically symmetrical potential, reconstructed from the data on the scattering of molecular beams. The more rigid behavior of the cold-compression curve of the molecular phase of hydrogen obtained by the method described above compared to the measurements[5] at pressures $P \gtrsim 3$ Mbar is in agreement with the conclusion drawn in Ref. 5 that a phase transition into the atomic phase occurs

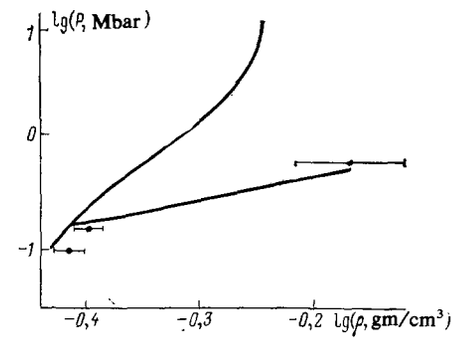

FIG. 3. The first and second shock adiabats of helium. The points with the confidence intervals are the measured values;[6] the solid line shows the calculation using TFC.[2]

in this region. We analyzed the experimental data[4] shown in Fig. 1 using a special technique which reveals the phase transition at $P = 70$ kbar on the cold-compression curve of hydrogen.

The reasonable agreement between the computed and experimental curves in Figs 1 and 2 (as well as Fig. 3, which shows the calculation of the first and second shock adiabats of He under conditions corresponding to the experimental conditions[6]) provides a basis for constructing wide-range equations of state of hydrogen, helium, and other noble gases.

These encouraging results suggest that the development of the microscopic approach to the study of compressibility on the basis of scattering data is promising. Important problems in this direction are the experimental study of the effects of nonadditivity of the interactions in the mega-gigabar pressure range and reconstruction from the scattering of molecular systems not only of the effective spherically symmetrical potentials, but also the complete potential-energy surface taking into account the anisotropy of the interaction and the dependence on the intra-atomic distances in molecules.

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S. I. Anisimov and Yu. V. Petrov. *Equation of state of molecular hydrogen in the megabar range, role of nonpair interactions.* The approximation of pair interatomic[1,2] or pair intermolecular interactions is often used to calculate the thermodynamic functions of molecular crystals, including the molecular-hydrogen crystal.[3,4] It is obvious that the pair-interaction approximation for molecules in a crystal is only the first term in the general cluster expansion of the energy of

the crystal, which takes into account the contribution of clusters consisting of not only two, but also three and more molecules. Using the cluster expansion, we write the internal energy of the crystal, relative to the energy of an isolated molecule E_0, in the form $E = E_2 + E_3$, where

$$E_2 = \frac{1}{2!}\sum_{i\neq j}\varepsilon_{ij}, \quad E_3 = \frac{1}{3!}\sum_{i\neq k\neq j}\varepsilon_{ijk}$$

are the energy of the pair and three-particle interactions, respectively; $\varepsilon_{ij} = E_{ij} - 2E_0, \varepsilon_{ijk} = E_{ijk} - \varepsilon_{ij} - \varepsilon_{ik} - 3E_0$ and, E_{ij}, E_{ijk} are the total energies of the many-electron systems of the molecules (i,j) and (i,j,k), respectively. The term E_3 gives the nonadditive three-particle correction to the energy of the crystal, due to pair interactions of molecules and increasing with the density and pressure. The closer approach of molecules caused by the higher density increases the overlapping of the orbitals of electrons on different molecules and, therefore, increases the nonadditive contribution to the energy of molecular interactions.[5]

We shall be concerned below with high pressures and low temperatures, to which the low-temperature static experiments (see for example Refs. 6 and 7), which provide the most direct and most accurate information on the cold-compression curve), refer. At high pressures the energy of the crystal can be separated with good accuracy into static and dynamic components and the vibrations of the lattice can be described in the harmonic approximation. This is also valid for crystals of hydrogen and light inert gases, which at normal pressure are quantum crystals.[8] In the range of interest to us, the energy of the lattice vibrations is a small fraction of the total energy of the crystal and can be calculated using the Debye model. If, however, the temperature is not low, as occurs, for example, in experiments with shock waves, then the problem of taking into account the thermal part of the pressure and determining the cold-compression curve from the experimental data becomes much more difficult.

As mentioned above, the static energy, which is calculated with the nuclei fixed in the equilibrium positions, makes the main contribution to the total energy. In the case of the molecular-hydrogen crystal, the previously introduced quantities E_{ij} and E_{ijk} are the energy of the electron-nuclear systems, consisting of two and three molecules, respectively, with fixed nuclei. The calculation of the energies of two- and three-molecule clusters requires the solution of four- and six-electron problems. Because of the peculiarities of a molecular crystal, in calculating the energy of two- and three-molecule clusters we used the valence bond approximation with a linear combination of 20 basis wave functions in the electronic wave function of two molecules and 37 basis functions for three molecules, taking into account the covalent and ionic bonds of electrons in the selected groups of molecules.[9-11] Two types of lattices were studied for molecular hydrogen: hcp with the molecular axes oriented parallel to the hexagonal axis and α-nitrogen type (fcc with the molecular axes oriented parallel to the spatial diagonals of the cube). In calculating E_3 we restricted the calculation to 150 clusters with the centers of the molecules located at the vertices of isosceles triangles the length of whose lateral side is

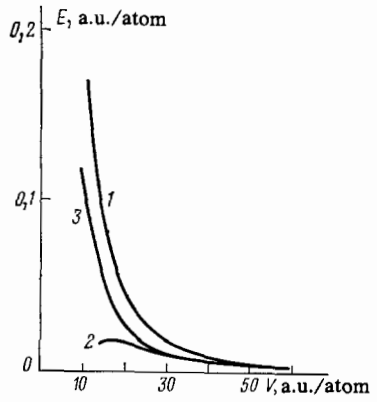

FIG. 1. The energy of a molecular hydrogen crystal as a function of the specific volume. The lattice is of the α-nitrogen type. 1) Pair interaction of molecules; 2) including three-particle interactions; 3) N-electron approximation ($N = 38$).

equal to the radius of the first coordination sphere. Among these 150 clusters, 24 clusters, the centers of whose molecules are at distances equal to the distance between the nearest neighbors, make the largest (negative) contribution.[1)] Calculations show that the effective pair potential is softer than the potential of the "bare" molecules in the density range studied and the pair potential differs markedly from the pair nature of the interaction of molecules with $v < 20$ a.u./atom. To estimate the range of applicability of the cluster expansion used, we solved in the same valence-bond approximation[12] the N-electron problem with $N = 38$ and for a nuclear configuration corresponding to the lattice of α-nitrogen. A comparison shows that for $v > 25$ a.u./atom the cluster expansion taking into account the triple interactions is a good approximation (Fig. 1). For smaller volumes clusters containing four and more molecules must be taken into account. The computed[12] and experimentally measured[7] curves of the pressure as a function of the specific volume are compared in Fig. 2. The agreement is good, especially considering the fact that the calculation was performed "from first principles." We note that the conclusion that nonpair

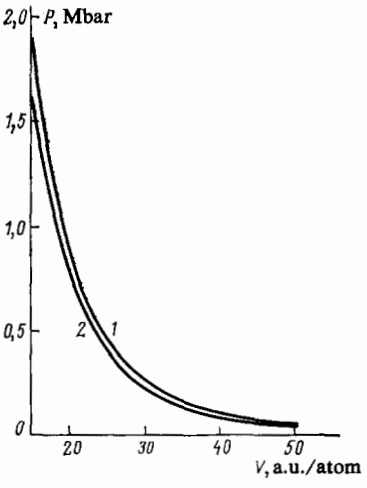

FIG. 2. Pressure of molecular hydrogen as a function of the specific volume. 1) Theory, 2) experiment.[7]

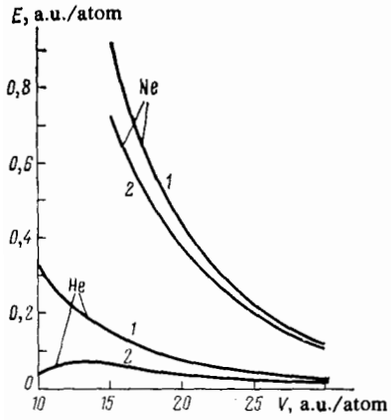

FIG. 3. Energy of fcc crystals of He and Ne as a function of the specific volume. 1) Pair-interaction approximation; 2) including three-particle interactions.

interactions play an important role in molecular hydrogen was also arrived at in Ref. 13 on the basis of an analysis of experimental data on dynamic compression.

The light inert gases—helium and neon—exhibit analogous behavior in the megabar range.[14] Calculations based on the cluster expansion of the energy of fcc lattices show that the nonadditive three-particle interaction of He and Ne molecules appreciably lowers the energy of the crystal as compared with the pair-interaction approximation (Fig. 3). This leads, correspondingly, to lower pressures.

[1)]We call attention to the fact that the contribution of linear three-particle clusters to the energy is negligibly small. The main contribution is linked to structures which are apparently not realized in the scattering experiments from which the interparticle potentials are often determined.

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L. V. Al'tshuler. *Results of and prospects for experimental studies of extremal states of matter.* The equations of state for extremal states of matter with high energy density are found from the result of static and dynamic experiments and their extrapolations to the periphery of phase diagrams, where simple theoretical models constructed from first principles are valid.

The basic thermodynamic characteristics of compressed and heated bodies are determined by the potential curves of "cold" interaction of particles and "Grüneisen functions," which reflect the thermal elasticity of matter. The experimental search for these dependences over a wide range of temperatures and densities was made possible by the use of strong shock waves as a tool in the physical studies.[1,2] Dynamic methods, developed independently in the Soviet Union and in the USA right after World War II are based on obtaining and recording states arising for short periods of time in sample targets struck by impactors. The measured quantities in shock-wave experiments are the velocity of the shock wave in the target and the velocity of the matter behind the wave front, determined from the velocity of the impactor. Through the equations expressing the conservation laws the kinematic characteristics of the wave determine the thermodynamic parameters of the compressed material: the pressure, density, and specific internal energy acquired from the impact. The measurements performed with different shock-wave velocities establish on the phase diagrams the trajectories characteristic shock-compression trajectories—the Hugoniot adiabats—with known values of the thermodynamic quantities.

Using the method of shock waves, by the beginning of the 1960s, pressures of the order of 1 TPa, which represent the upper limit of absolute laboratory measurements of the dynamic compressibility, were achieved in the Soviet Union using explosive devices which smoothly accelerated iron impactors up to velocities of ~15–18 km/sec. Half of this range has now been achieved in the USA, where systematic studies are performed with a two-stage light-gas cannon, which imparts a velocity of up to 8.5 km/sec to a tantalum impactor.[3]

Further progress toward the limits of the theoretical description has been achieved in experiments with shock waves in the near zone of strong undeground explosions. Under these conditions, with the help of γ emitters built into an aluminum sample, in Ref. 4 wave and mass velocities were measured and the compressibility of aluminum at 1 TPa was determined. A different, less accurate method was used in Ref. 5 to obtain the parameters of the shock-compression of molybdenum at 2 TPa. The main result[6–8] of the studies in the tera-Pascal pressure range was the determination of the comparative compressibility of many metals. In the experiments set up for these purposes, the velocities of the shock wave were recorded as the wave passed through successive layers of different metals. The interpretation of these experiments requires knowledge of the shock adiabat of one of the metals. In studies carried out in the Soviet