POSSIBLE PHASE TRANSITION IN SOLID PARAHYDROGEN

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The results of an investigation of the thermal expansion and of the compressibility of solid parahydrogen under pressure suggest the existence of a phase transition in the pre-melting region.

In a study of the thermal expansion of solid parahydrogen in the pre-melting region at a pressure of 30 atm, we observed jumpwise changes in the volume. The positions of the changes depended on the direction of the temperature variation (hysteresis) and on the prior history of the solidified gas. The experimental procedure was similar to that described in [1]. The measuring cell used in the present work differed from that in [1] principally in its larger working volume; this improved appreciably the reproducibility of the results. The para-composition of the employed samples was 98 ± 0.5%. The figure shows the temperature dependence of the molar volume V of solid parahydrogen, obtained from three series of measurements. The hydrogen crystallization took 40 minutes. The volume jump takes place in the interval 13.7 - 14.2°K and its value (averaged over the results of 12 experiments) is 0.15V. The samples obtained with slower crystallization exhibit a larger hysteresis, and the upper temperature of the jump can differ by only 0.2 - 0.3 °K from T_m = 14.8°K. Preliminary investigations of the thermal expansion at 150 atm and measurements of the compressibility have also revealed jumps of the volume of solid parahydrogen.

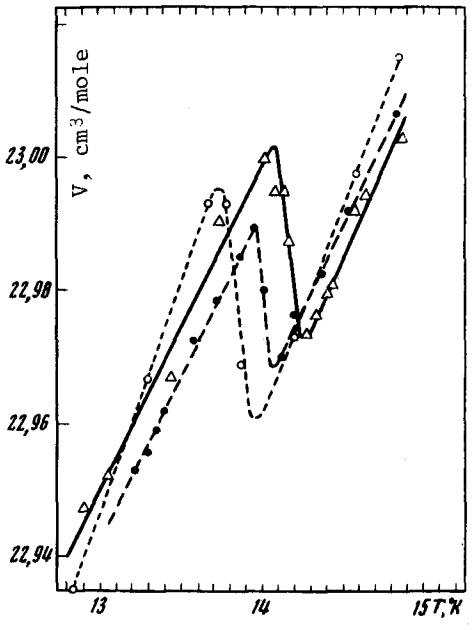

Fig. 1. Molar volume of parahydrogen at P = 31 atm vs temperature: triangles and dark circles - rising T, light circles - dropping T.

It is natural to interpret the observed phenomena as manifestations of a first-order phase transition in solid parahydrogen. Somewhat unusual for a simple molecular crystal is the decrease in volume on going from the low-temperature phase to the high-temperature one. The procedure of our measurements was such [1] that changes in the volume were accompanied by plastic flow of the sample. It is known [2] that deformation of the sample can shift the transition temperature appreciably. This is why, in particular, the equilibrium transition temperature cannot be determined sufficiently accurately by our method.

Parahydrogen was previously investigated in the temperature and pressure range of interest to us in [3 - 5]. An increase of the density with increasing temperature in the pre-melting region was noted in [3] and was attributed to a negative coefficient of thermal expansion. These results can be equally well explained, however, as due to the existence of a first-order phase transition. The non-reproducibility and anomalously large absorption of ultrasound in solid parahydrogen, recently observed by Wanner and Meyer, can also be connected with the existence of a phase transition. At the same time, measurements of the specific heat [5] and of the sound velocities [4] in solid parahydrogen under pressure revealed no phase transition. It is possible that, owing to the very small difference between the densities of the phases, the corresponding difference between the speeds of sound and the specific heats does not exceed the experimental errors. Under such conditions, the temperature dependence of the speed of sound may not sense the phase transition. It is possible to observe a phase transition in measurements of the specific heat $C = \Delta Q/\Delta T$ if the calorimetric heating ΔT spans the transition temperature or a region immediately adjacent to it. It is seen from Figs. 2 and 3 of [5] that the values of the specific heat in the region of temperatures and pressures of interest to us are determined at points that are not too close to one another, and the phase transition might have escaped observation. We plan to investigate this phenomenon in detail at pressures up to 200 atm.

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GIANT QUANTUM OSCILLATIONS OF SECOND HARMONIC OF SOUND IN BISMUTH

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Generation of the second harmonic of sound in bismuth was observed, as well as giant quantum oscillations of the second harmonic of sound under the condition $\varepsilon_F \gg \hbar\Omega \gg kT$ (ε_F is the Fermi energy, Ω the cyclotron frequency, and T the absolute temperature). The dependence of the second-harmonic power on the power of the sound at the fundamental frequency is determined.

Nonlinear phenomena in piezo-semiconductors, produced by propagation of acoustic waves of finite intensity, have been the subject of an appreciable number of investigations (e.g.[1 - 3]). The mechanism of these phenomena is associated with the so-called concentration nonlinearity - the capture of the carriers by deep potential wells connected with the motion of the sound wave and the depletion of carriers from the remainder of the volume. As a result, both the sound velocity and its absorption depend on the intensity of the acoustic waves.

Such a mechanism can apparently not be realized in pure metals and semimetals if $K\ell \gg 1$ (K is the wave vector of the sound and ℓ is the electron mean free path), since the Fermi energy of the electrons is much larger than the depth of the potential wells produced by the sound wave. When a wave with $K\ell \ll 1$ passes through the metal, the interaction between the acoustic waves and the electrons, which has a deformation nature in metals, decreases strongly and the conditions for the existence of the nonlinearity are not realized. The possible existence of a nonlinearity mechanism connected with the distortion of the electron distribution function by the sound wave was discussed in [4 - 6]. Such a mechanism, as shown in [6], should lead to a number of phenomena of clearly pronounced nonlinear character in metals and semimetals, such as the generation of the second harmonic of the acoustic wave, the dependence of the intensity of this harmonic on the magnetic field, the onset of combination frequencies, and also giant quantum oscillations of the second harmonic when the condition

$$\varepsilon_F \gg \hbar\Omega \gg kT$$

is satisfied (ε_F is the Fermi energy, Ω the cyclotron frequency, and T the absolute temperature).

The purpose of our experiments was to observe these phenomena in pure bismuth. The samples were cut by the electric spark method from a bulky single crystal and were in the form of disks 6 - 8 mm in diameter and 1 - 2 mm thick. The plane of the cut was perpendicular to the X or Y axis of the crystal (X - binary, Y - bisector). The resistance ratio characterizing the purity of the sample was R(300°K)/R(4.2°K) = 300.

The sound was excited and registered by a pulsed method using longitudinal-type sound converters with single-crystal $LiNbO_3$. To obtain maximum sound power in the sample at a given generator power, the coaxial-line and converter impedances were matched with the aid of lumped capacitors. The generated first harmonic frequency of the sound was 235 MHz, and reception was at 470 MHz.

Figure 1 shows the second-harmonic signal amplitude (in arbitrary units) against the magnetic field intensity, at the output section of the sample, for the orientation