

tal errors) to the wavelength at that place of the transient wave, where  $\omega = 0$ .

A dispersion curve was calculated from the transient wave of Fig. 1(a), respecting the change in sign of the phase velocity (and, hence,  $\omega$ ). The result is shown in Fig. 1(b). The dispersion curve cuts the wave-number axis with negative slope at the point corresponding to the wave number  $k_{st}$  at zero phase velocity in the transient wave.

The wave shown in Fig. 1(a) is similar to the wave found earlier in 60% neon, 40% hydrogen mixture<sup>2</sup> where, however, the asymptotic behavior was that of a forward wave. It may be concluded from these results that the normal and anomalous dispersion curves found by Pfau and Rutscher,<sup>3</sup> in the same mixture but with different ratios of partial pressures, can be ascribed to the same physical phenomenon. As the backward waves in inert gases in this pressure region can be interpreted as ionization waves,<sup>4</sup> it is possible to extend this interpretation to the forward waves found in the mixture and in pure hydrogen, too, though no explanation of the forward phase velocity has been given as yet.

On the other hand, the dispersion curves for backward and forward waves in low-pressure arcs reported recently by Barrett and Little<sup>5</sup> cannot be interpreted by means of a dispersion curve cutting the  $k$  axis: Their forward waves

evidently belong—in agreement with the interpretation given in reference 5—to a different physical process.

The dispersion curve in Fig. 1(b), as well as the transient wave with  $\omega = 0$ , demonstrates clearly the connection between moving and standing striations, pointed out, e.g., by Klarfeld,<sup>6</sup> and recently on the basis of an extrapolation of dispersion measurement by Pfau and Rutscher.<sup>3</sup> The standing periodic pattern corresponds to the point where the dispersion curve cuts the wave-number axis. If the minimum attenuation occurs just for this point  $k_{st}$ , a transient wave with  $\omega = 0$  in its center is observed after a pulse disturbance.

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## CRYSTAL STRUCTURE OF NORMAL HYDROGEN AT LOW TEMPERATURES\*

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In 1930 Keesom, De Smedt, and Mooy<sup>1</sup> first determined the crystal structure of parahydrogen by x-ray diffraction. Their measurements at liquid-helium temperatures gave the hexagonal closest packed structure. Later confirmations of this structure were reported by Van Kranendonk and Gush<sup>2</sup> from an analysis of the infrared spectrum of the solid, and by Kogan, Bulatov, and Yakimenko<sup>3</sup> by x-ray diffraction.

Recently Clouter and Gush,<sup>4</sup> while studying the infrared spectrum of solid normal hydrogen in the range of liquid-helium temperatures, observed effects which indicated that the solid changed its crystal structure around 1.5°K. As described by them, one feature of the infra-

red spectrum is the  $S_1(0)$  line which arises from the quadrupolar induction effect. The intensity of this line is proportional to the square of the sum of the dipole moments which are induced in all neighboring molecules by the quadrupole field of the absorbing molecule. In parahydrogen the sum would vanish if the absorbing molecule were located at a center of inversion symmetry. The fact that the  $S_1(0)$  line is observed in solid parahydrogen is in accord with the observation that the structure is hexagonal closest packed, since, in this structure, the molecules are located at lattice points which are not centers of symmetry. In normal hydrogen the intensity of the  $S_1(0)$  line is modified by the ortho

molecules, but the presence or absence of the line is determined by the location of the para molecules with respect to a center of symmetry.

For  $n\text{-H}_2$  Clouter and Gush observed a strong  $S_1(0)$  line above  $1.5^\circ\text{K}$ , but at lower temperatures the line intensity almost disappeared. This and other features of the spectrum indicated that a structure change to one possessing inversion symmetry took place upon cooling. The temperature of the transition was found to decrease with decreasing ortho-para ratio, a dependence similar to that of the anomaly in nuclear magnetic resonance<sup>5</sup> and of the  $\lambda$  anomaly in specific heat.<sup>6,7</sup> To gain more insight into the nature of the transition, we undertook an investigation by x-ray diffraction of the structure of  $n\text{-H}_2$  at liquid-helium temperatures.

The apparatus used was from our earlier helium studies.<sup>8</sup> The hydrogen sample was frozen inside a short beryllium cell of 0.8-mm bore by 0.4-mm wall. Each end of the cell was connected to a small container of liquid helium which was fed from the main Dewar. Surrounding the cell assembly were two copper radiation shields with thin aluminum windows. One shield was cooled by liquid helium and the other by liquid nitrogen. From the earlier work it was estimated that the portion of sample exposed to x rays was about  $0.04^\circ\text{K}$  warmer than the liquid helium refrigerant. The sample was oscillated through an angle of  $44^\circ$  and, with filtered iron radiation, photographs were taken by a cylindrical camera.

The hydrogen was drawn from a lot which had been in our laboratory for 12 years and was assumed to be of normal ortho-para ratio. In one experiment, when a sample containing a lesser ortho-para ratio was desired, the gas was first passed over a  $\text{Cr}_2\text{O}_3$  catalyst held at  $75^\circ\text{K}$  which reduced the ortho concentration from 75 to about 50%. To insure that the sample cell would contain an adequate amount of solid, our procedure was first to introduce into the cell at liquid-nitrogen temperature hydrogen gas at 100 atm and, while holding this pressure, to add liquid helium to the cryostat and quickly cool the sample to the desired temperature. From previous experience it was anticipated that the 0.15-mm i.d. filling tube would plug with solid  $\text{H}_2$  well before the cell had filled. Depending on when the plug formed, it was estimated that the cell would be 30 to 90% full of solid  $\text{H}_2$  and at approximately zero pressure.

The diffraction photographs showed a series

Table I. Hcp data from seven photographs above  $1.30^\circ\text{K}$ .

$hkl$	$d(\text{obs})$ ( $\text{\AA}$ )	$d(\text{calc})$ ( $\text{\AA}$ )
100	3.255	3.257
002	3.052	3.052
101	2.875	2.873
$a = 3.761 \pm 0.007 \text{ \AA}$ , $c = 6.105 \pm 0.011 \text{ \AA}$ , $c/a = 1.623$		
$\bar{V} = 22.52 \text{ cc/mol}$		

of spots, not continuous lines, indicating that the solid was a conglomeration of small crystals. From our examination of 10 photographs made under various conditions, a change in the crystal structure of  $n\text{-H}_2$  was observed at low temperature. The structure is hexagonal close packed from  $4^\circ\text{K}$  to about  $1.3^\circ\text{K}$  and transforms below this temperature to face-centered cubic. To verify that the transition temperature decreases with decreasing ortho-para ratio, the ortho concentration was reduced as described above and the transition temperature was found to decrease apparently to below  $1.25^\circ\text{K}$ , the low-temperature limit of the cryostat, since the structure remained hexagonal.

In Tables I and II are listed, for each structure, the average values of the observed interplanar spacings  $d$ , the cell dimensions  $a$  and  $c$ , and the molar volume  $\bar{V}$  derived therefrom. In the case of the hexagonal structure, the cell dimensions were determined from a least-squares fit of the three interplanar spacings. Values of  $d(\text{calc})$  were computed from the fitted dimensions.

From pycnometer data listed by Woolley, Scott, and Brickwedde,<sup>9</sup> the molar volume of  $n\text{-H}_2$  at  $p = 0$  and  $T = 1.3^\circ\text{K}$  is computed to be  $22.58 \text{ cc/mol}$ , in excellent agreement with present measurements. Within experimental error, the computed molar volumes for the two structures in Table I and II are not significantly dif-

Table II. Fcc data from three photographs between  $1.25$  and  $1.30^\circ\text{K}$ .

$hkl$	$d(\text{obs})$ ( $\text{\AA}$ )	$a$ ( $\text{\AA}$ )
111	3.067	5.312
200	2.649	5.298
220	1.883	5.325
Avg. cell edge = $5.312 \pm 0.010$		
$\bar{V} = 22.57 \text{ cc/mol}$		

ferent.

A more complete and extensive study is underway in which we are investigating the effects of pressure, temperature, ortho-para ratio, and isotopic species on the transition.

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## EFFECTS OF HIGH MAGNETIC FIELDS ON THE ULTRASONIC VELOCITY AND ATTENUATION IN Nb-25% Zr

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In this Letter we report the observation of changes in the velocity and attenuation of ultrasonic waves propagating in the superconducting and normal states of Nb-25% Zr, caused by the presence of a high dc magnetic field. These changes are abrupt near the upper critical field  $H_{c2}$ , determined by magnetization measurements.<sup>1</sup> The conventional interpretations of the changes in the ultrasonic attenuation<sup>2</sup> and the velocity<sup>3</sup> near  $H_{c2}$  do not apply to this high-field superconductor because the effects of the magnetic field necessary to destroy superconductivity are large.<sup>4</sup> On the other hand, the velocity and attenuation changes observed in the superconducting state agree with the predictions of the Alpher-Rubin<sup>5</sup> (AR) theory which was originally derived for impure metals in the normal state. This agreement is particularly good for sound waves in the megacycle range, although deviations are observed at higher frequencies. As expected, the AR theory also accounts for the results in the normal state.

The macroscopic theory of AR<sup>5</sup> predicts that the velocity  $V_s$  of a sound wave of frequency  $\omega$  propagating in a metal with electrical conductivity  $\sigma$  increases by  $\Delta V_s$  in the presence of a magnetic field  $H$ . For a shear wave

$$\frac{\Delta V_s}{V_s} = \frac{\mu H^2 \cos^2 \theta}{8\pi \rho V_s^2 (1 + \beta^2)}, \quad (1)$$

where  $\mu$  is the permeability,  $\rho$  is the density of the metal,  $\theta$  is the angle between  $\vec{H}$  and the wave vector  $\vec{q}$  of the sound, and

$$\beta = c^2 \omega / 4\pi \sigma V_s^2. \quad (2)$$

Rodriguez<sup>6</sup> has shown that Eq. (1) can be derived from a microscopic theory in the case of impure metals in which  $ql, \omega_c \tau, \omega \tau \ll 1$ , where  $l$  is the electron mean free path,  $\omega_c$  is the cyclotron frequency, and  $\tau$  is the electron relaxation time. These conditions are well satisfied in the normal state of our Nb-25% Zr sample. Starting from the assumptions of AR one can show that the amplitude of sound wave decays with the distance  $x$  as  $e^{-\alpha x}$  where, for a shear wave,

$$\alpha = \frac{\sigma H^2 \mu^2 \beta^2 \cos^2 \theta}{2\rho V_s c^2 (1 + \beta^2)} \text{ cm}^{-1}. \quad (3)$$

For a longitudinal wave the  $\cos^2 \theta$  term in Eqs. (1) and (3) is replaced by  $\sin^2 \theta$ . Equation (1) has been tested experimentally in a number of metals,<sup>7</sup> in the normal state, and has been found to hold when  $\beta \ll 1$ . When  $\beta \geq 1$  the sound velocity increases quadratically with  $H$ , but the increase is somewhat different, in some cases, from that given by the AR theory. To our knowledge, Eq. (3) has not been previously tested experimentally.