

TABLE II. Parameters derived from the spectra.

	$B_e$	$\alpha$
$\text{Br}^{79}\text{Cl}^{35}$	$4570.92 \pm 0.04$ Mc/sec.	$23.22 \pm 0.03$ Mc/sec.
$\text{Br}^{81}\text{Cl}^{35}$	$4536.14 \pm 0.04$	$22.95 \pm 0.03$
$\text{Br}^{79}\text{Cl}^{37}$	$4499.84 \pm 0.04$	$21.94 \pm 0.03$
$\text{Br}^{81}\text{Cl}^{37}$	$4365.01 \pm 0.04$	$21.67 \pm 0.03$
	$eqQ(\text{Br}^{79}) = +876.8 \pm 0.9$ Mc/sec.	
	$eqQ(\text{Br}^{81}) = +732.9 \pm 0.5$	
	$eqQ(\text{Cl}^{35}) = -103.6 \pm 0.15$	
	$eqQ(\text{Cl}^{37}) = -81.14 \pm 0.15$	
	$r_e = 2.138(10)^{-8}$ cm	
	$\mu = 0.57 \pm 0.02$ Debye units	

variation from one isotopic species to another suggests that these are random experimental errors.

The value of the dipole moment has not been obtained by exact computation but has been estimated on the assumption that, neglecting quadrupole effects, the dipole moment lies between that obtained from the largest and the smallest observed Stark coefficients, and that the best value is given by the average of the observed Stark coefficients.

The values of the vibrational stretching coefficient for the  $\text{Cl}^{37}$  isotopic species have been obtained from the known variation of  $\alpha$  with the  $\frac{3}{2}$  power of the reduced mass, and used to obtain the equilibrium rotational constants. These lead to two semi-independent values for the chlorine mass ratio. The ratio  $m(\text{Cl}^{35})/m(\text{Cl}^{37})$  is  $0.945987 \pm 0.000008$  for the  $\text{Br}^{79}\text{Cl}^{35}$ ,  $\text{Br}^{79}\text{Cl}^{37}$  pair, and  $0.945986 \pm 0.000008$  for the  $\text{Br}^{81}\text{Cl}^{35}$ ,  $\text{Br}^{81}\text{Cl}^{37}$  pair. This is to be compared with the value  $0.945980 \pm 0.000005$  obtained from<sup>4</sup>  $\text{ICl}$  and  $0.9459775 \pm 0.000004$  obtained in<sup>5</sup>  $\text{ClF}$ , and as pointed out by Townes, Merritt, and Holden<sup>4</sup> to be contrasted with the mass spectrographic results  $0.945944 \pm 0.000007$ .

The values for  $m(\text{Br}^{79})/m(\text{Br}^{81})$ ,  $0.975218 \pm 0.000028$  for the  $\text{Br}^{79}\text{Cl}^{35}/\text{Br}^{81}\text{Cl}^{35}$  pair and  $0.975210 \pm 0.000028$  for the  $\text{Br}^{79}\text{Cl}^{37}$ ,  $\text{Br}^{81}\text{Cl}^{37}$  pair are considerably lower than the mass spectrographic values<sup>6</sup> of  $0.975316 \pm 0.000005$ . A recalculation of this ratio in<sup>7</sup>  $\text{BrF}$  yields  $0.975168 \pm 0.000068$ .

The ratio of the chlorine quadrupole moment ratios  $eqQ(\text{Cl}^{35})/eqQ(\text{Cl}^{37})$ ,  $1.2768 \pm 0.004$  is in better agreement with the ratio obtained from measurements of the moments in atomic beams  $1.279 \pm 0.00265$  than was found<sup>5</sup> for  $\text{ClF}$ ,  $1.2704 \pm 0.004$ . The ratio for the bromine quadrupole coupling appears to be in excellent agreement with that obtained in other compounds. Professor B. P. Dailey, in private conversation, has pointed out that the magnitudes of the coupling coefficients for chlorines are considerably larger than expected, and that to a lesser extent the bromine coupling coefficients are also large.

\* This document is based on work performed for the AEC by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, at Oak Ridge, Tennessee.

<sup>1</sup> H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.* **56**, 620 (1934).

<sup>2</sup> J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 97 (1948).

<sup>3</sup> J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 627, 1204 (1948).

<sup>4</sup> Townes, Merritt, and Wright, *Phys. Rev.* **73**, 1334 (1948).

<sup>5</sup> Gilbert, Roberts, and Griswold, *Phys. Rev.* **76**, 1723 (1949).

<sup>6</sup> R. Ogata, *Phys. Rev.* **75**, 200 (1949).

<sup>7</sup> Smith, Tidwell, and Williams, *Phys. Rev.* **77**, 420 (1950).

## Transport Rates of the Liquid He II Film over Various Surfaces

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OUR recent letter<sup>1</sup> describing a new method for measuring transport rates of the He II film reported that the rate over copper was significantly higher than that over glass. Owing to the fact that the transport rate was found to be strongly dependent on surface treatment, numerical values were not given, it being felt that details might await the publication of a full

report. While the letter was in press, however, Mendelssohn and White<sup>2</sup> reported measurements of the transport rate over nickel and platinum which demonstrated a dependence on substrate and surface treatment.

It seems worth while, therefore, to point out that we have found the effect to be quite general and that both metals and dielectrics show rates different from each other and from glass. In fact, of all of the substances which we have measured, glass shows the smallest rate at any given temperature, as is apparent from Table I below. In each experiment the rate over glass was meas-

TABLE I. Transport rate in  $\text{cm}^2/\text{cm-sec.} \times 10^8$ .

	1.3°	1.5°	1.8°	2.0°
Pyrex glass	7.6	7.5	—	—
Lucite	14.4	16.6	11.5	—
Stainless steel	10.4	9.7	6.8	3.3
Lead	33.3	31.1	26.6	16.5
Cold-rolled steel	10.5	—	—	—
Machined copper	14.8	14.8	12.4	7.9
Polished copper	23.0	19.8	14.7	7.1
Etched copper	51.2	49.0	40.0	24.8
Etched copper, oxidized	26.0	24.8	20.4	13.7

ured for comparison purposes and to be sure that there was no significant contamination arising from gases solidified on the transfer surfaces.

It seemed of particular interest to determine whether or not the rate over a metal in the superconducting state was different from the normal state, the temperature being constant. The experiment was tried using lead, the normal state being achieved by the application of a sufficiently strong transverse magnetic field. While there appeared to be small systematic differences at various temperatures, further investigations (now under way) will be necessary to determine whether these are real. The same remarks apply to iron, transversely magnetized and in the non-magnetized state.

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‡ Assisted by ONR, Research Corporation, and The Linde Air Products Company.

<sup>1</sup> H. A. Boorse and J. G. Dash, *Phys. Rev.* **79**, 734 (1950).

<sup>2</sup> K. Mendelssohn and G. K. White, *Nature* **166**, 27 (1950).

## Displacement of Oxygen in $\text{BaTiO}_3$

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ATTEMPTS to explain the ferroelectric character of  $\text{BaTiO}_3$  in terms of ionic displacements<sup>1-7</sup> have usually concentrated attention on the Ti ion. Megaw<sup>1</sup> has pointed out that if one assumes the Goldschmidt ionic radii, the Ba ions at the corners of the unit cell are slightly too large to fit into a close-packed perovskite structure; consequently the lattice is expanded and the Ti ions, at the body centers, are free to move through small distances. In such a model each oxygen ion, at a face center, is squeezed between four Ba ions, but is free to move at right angles to the plane of Ba ions, toward the Ti ions. Devonshire<sup>6</sup> has estimated the forces on the Ti and O ions following Born's treatment, with the result that the Ti ion is definitely bound to its symmetrical position, but the force restoring an oxygen ion to its symmetrical position is much smaller, and of uncertain sign. It therefore appears that any theory of  $\text{BaTiO}_3$  based on this model must consider displacement of the oxygen ions as being at least as effective a cause of polarization as is Ti displacement.

A model in which ionic polarization arises chiefly from the oxygen ions is capable of explaining in a very simple way the observed three phase transitions, and predicts the correct magnitude of the transverse electrostriction in the tetragonal phase. Each unit cell contains three oxygen ions,  $O_x$ ,  $O_y$ ,  $O_z$ , which are

free to move in the  $x$ -,  $y$ -, and  $z$ -directions respectively. Starting with cubic BaTiO<sub>3</sub> above 120°C, and cooling the crystal, the effect of the mismatch in ionic size as the lattice contracts is first to squeeze one of the oxygens, say O<sub>z</sub>, out of its plane of Ba ions. This results in a spontaneous polarization and a deformation of the crystal, the symmetry becoming tetragonal. Contraction in the directions at right angles to the polarization occurs, since the Ba ions, which were pressing against the O<sub>z</sub> ion, can now come together by a small amount proportional to the square of the O<sub>z</sub> displacement  $z$ . A simple geometrical argument based on hard spheres in contact gives for the transverse contraction  $-\Delta a/a = (z/a)^2$ , where " $a$ " is the lattice constant. The polarization  $P_{0z}$  due to displacement of O<sub>z</sub> is  $2\epsilon z a^{-3}$ , so that the transverse contraction becomes

$$-\Delta a/a = (a^4/4e^2)P_{0z}^2 = 3.8 \times 10^{-12} P_{0z}^2.$$

Experimentally,<sup>8</sup>  $-\Delta a/a$  is found to be accurately proportional to the square of the total polarization, with a coefficient of  $1.2 \times 10^{-12}$ . Thus, if  $P_{0z}$  represents 56 percent of the total polarization, the transverse electrostriction is given correctly.

The displacement of O<sub>z</sub> relieves the instability of the lattice to a certain extent; as we further cool the crystal, a second group of oxygens, say the O<sub>y</sub>, get squeezed out of their symmetrical positions, and the polarization now has equal components in the  $z$  and  $y$  directions, the crystal distorting to orthorhombic symmetry. On further cooling, the O<sub>x</sub> ions are squeezed out of place, resulting in a net polarization directed toward the diagonal of the original cube, and the symmetry becomes rhombohedral. All of these changes of phase and polarization direction are observed experimentally.<sup>8</sup>

Certain obvious refinements of this model would change the above numerical estimates, but it is clear that we get a qualitative understanding of two of the most puzzling features of BaTiO<sub>3</sub>, namely the existence of three phase transitions with shifts of the direction of spontaneous polarization, and the very large electro-mechanical coupling.

I am indebted to Professor E. P. Wigner and Dr. B. T. Matthias for helpful discussions.

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<sup>2</sup> Rushman and Strivens, *Trans. Faraday Soc.* **42A**, 231 (1946).  
<sup>3</sup> Mason and Matthias, *Phys. Rev.* **74**, 1622 (1948).  
<sup>4</sup> G. H. Jonker and J. H. van Santen, *Science* **109**, 632 (1949).  
<sup>5</sup> A. F. Devonshire, *Phil. Mag. (Series 7)* **40**, 1040 (1949).  
<sup>6</sup> P. W. Anderson, *Phys. Rev.* **78**, 341 (1950).  
<sup>7</sup> J. C. Slater, *Phys. Rev.* **78**, 748 (1950).  
<sup>8</sup> W. J. Merz, *Phys. Rev.* **76**, 1221 (1949).

### On the Hyperfine Structure of Hydrogen and Deuterium\*

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A NEW determination of the hyperfine structure separation of both hydrogen and deuterium in the  $^2S_{1/2}$  state has been made by the atomic beam method. The new values are, for several reasons, of considerably greater precision than those previously reported.<sup>1</sup> The r-f circuit which produced the oscillating magnetic field was arranged so that no Doppler effect<sup>2</sup> could occur to shift or broaden the lines. The deflecting fields, which were set up by current carrying conductors, were sufficiently remote from the transition region to have a negligible effect on the field in that region. The transition field itself was extremely stable since the transitions were observed in the permanent residual laboratory field of about 0.3 gauss. The Pirani gauge detector, of a design proposed by Zacharias,<sup>3</sup> was extremely fast so that no very great demands were put on the stability of the frequency source, and it was possible to accumulate a large body of significant data.

In the case of hydrogen, the  $\sigma$ -line  $(1, 0) \leftrightarrow (0, 0)$  and the two  $\pi$ -lines  $(1, 1) \leftrightarrow (0, 0)$  and  $(1, 0) \leftrightarrow (1, -1)$  were observed. The  $\sigma$ -line gives the hyperfine structure separation,  $\nu_H$ , directly after the application of a small quadratic correction of about 0.3 kc in these measurements. The difference in the frequencies of the two  $\pi$ -lines is identically equal to  $\nu_H$ . All frequency measurements were made in terms of the 5 Mc signal from WWV. For several runs, each of which consisted of many measurements of the line centers, the following results were obtained:

Run	Method	$\nu_H \times 10^{-6} \text{ sec.}^{-1}$
1	$\sigma$ -line	1420.4056 $\pm$ 0.0010
2	$\sigma$ -line	1420.4053 $\pm$ 0.0005
2	$\pi$ -lines	1420.4051 $\pm$ 0.0016
3	$\sigma$ -line	1420.4048 $\pm$ 0.0005

Weighted Mean 1420.4051  $\pm$  0.0003

The stated uncertainty is about twice the usual probable error.

Deuterium has two nearly field independent, unresolved  $\pi$ -lines at weak fields,  $(\frac{3}{2}, \frac{1}{2}) \leftrightarrow (\frac{1}{2}, -\frac{1}{2})$  and  $(\frac{3}{2}, -\frac{1}{2}) \leftrightarrow (\frac{1}{2}, \frac{1}{2})$ . The frequency separation of these lines is  $2g_I\mu_0H/\hbar$  which in our case is about 0.4 kc. Since the probability of each of these transitions is the same, and since atoms in the states  $(\frac{3}{2}, \frac{1}{2})$  and  $(\frac{3}{2}, -\frac{1}{2})$  have substantially identical trajectories in the apparatus as have also atoms in the states  $(\frac{1}{2}, \frac{1}{2})$  and  $(\frac{1}{2}, -\frac{1}{2})$ , the center of gravity of the observed line, of about 22 kc half width, can be used to fix  $\nu_D$  without ambiguity. From numerous measurements on these lines and from less precise measurements on other  $\pi$ -lines to determine the quadratic correction, we find:

$$\nu_D = (327.38424 \pm 0.00014) \times 10^{-6} \text{ sec.}^{-1}.$$

From these results, the experimental value of the ratio of  $\nu_H/\nu_D$  is:

$$(\nu_H/\nu_D)_{\text{exp}} = 4.3386484 \pm 0.0000020.$$

This value may be compared to the theoretical value of the ratio which is given by the expression:

$$(\nu_H/\nu_D)_{\text{theor}} = 4/3(m_H/m_D)^3(\mu_H/\mu_D)$$

where  $m_H$  and  $m_D$  are the reduced masses of an electron in hydrogen and deuterium respectively. Using the value of  $\mu_H/\mu_D$  determined by Smaller, Yasaitas, and Anderson,<sup>4</sup> and  $m_H/m_e = 1835.979 \pm 0.056$ <sup>5</sup>

$$(\nu_H/\nu_D)_{\text{theor}} = 4.3393876 \pm 0.0000008.$$

The discrepancy between the experimental and theoretical ratio may be written as:

$$(\nu_H/\nu_D)_{\text{exp}} = (\nu_H/\nu_D)_{\text{theor}} [1 - (1.703 \pm 0.007) \times 10^{-4}].$$

This result agrees with the less accurate result of Nafe and Nelson.<sup>1</sup>

From theoretical considerations of the effects of internal nuclear motion on the hyperfine structure of deuterium, Low<sup>6</sup> obtains:

$$(\nu_H/\nu_D) = (\nu_H/\nu_D)_{\text{theor}} [1 - (1.83 \pm 0.22) \times 10^{-4}].$$

In view of the large uncertainty in the theoretical calculation, it is not possible to draw a significant conclusion from the disagreement between the observed and calculated values. However, the accurately known discrepancy between the observed and calculated values of the ratio of the  $\nu$ 's makes possible a careful investigation of the structure of the deuteron.

The fine structure constant,  $\alpha$ , may be found<sup>7</sup> from the known value of  $\nu_H$  and from the known value of  $\mu_H/\mu_0$ . The new value of  $\nu_H$  does not significantly alter the previously stated value of  $\alpha$ . However, the present precision in  $\nu_H$  is greater than that of any other quantity in the theoretical relationship. It is of interest to note that a very much improved precision in the value<sup>8</sup> of  $\mu_H/\mu_0$ , new calculations for the diamagnetic fields at a nucleus in a molecule,<sup>9</sup> a new<sup>10</sup> fourth-order correction of the spin magnetic moment of the electron, and a very much improved value of the velocity of light<sup>11</sup> now suggest the possibility of obtaining  $\alpha$  to a