

levels with a much smaller activation energy. This effect, that the 0.23-ev acceptor levels disappear on annealing and that in their place acceptor levels appear with a smaller activation energy, has been found in all the samples examined.

Experiments carried out to determine the density of the different levels as a function of the annealing time at temperatures of 450°C and below, indicate that the density N_0 of the new, low-lying, acceptor levels first increases rapidly with increasing annealing time, and then reaches a maximum followed by an exponential decrease. The total density of acceptor levels first remains constant or decreases very slowly. After the maximum in N_0 has been reached, the decrease is more rapid and exponential, the exponent being the same as in the decrease of N_0 , giving a constant ratio between the densities of the low-lying levels and of the 0.23-ev level. Curve *b* of the figure refers to an annealing time such that N_0 is about maximum.

¹ F. van der Maesen and J. A. Brenkman, Philips Research Repts. 9, 225 (1954).

Magnetic Hyperfine Structure in Bismuth Hydride and Deuteride

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APPLYING a spectroscopic immersion method, described earlier,¹ we have succeeded in resolving the hyperfine structure of the low rotational states $J=1, 2,$ and 3 in the red spectral region of BiH and BiD corresponding to the transition $A\ ^1\Sigma - ^1\Pi$. The hfs exhibited is, as far as we know, the only case of molecular magnetic hfs known in the optical region²; moreover, it furnishes a simple case not encountered in the microwave region either. The following report gives a brief description and a more detailed discussion will be

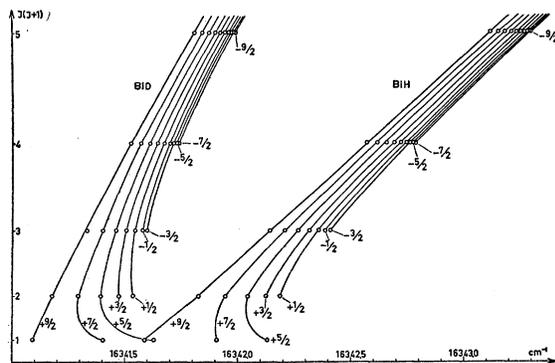


FIG. 1. Fortrat diagram of the hfs in the Q branches of the BiH and BiD spectrum at $\lambda=6118$ Å. The curves are drawn according to the magnetic quantum numbers M_I of the Bi nucleus.

given later. Figure 1 shows a short region of the Q branches of the (0,0) bands in BiH and BiD on a scale of $J(J+1)$. This type of Fortrat diagram is useful as the Q branches are represented by nearly straight lines, as expected from their calculated central positions, not including hfs:

$$\text{BiH: } Q(J) = 16\,341.628 + 5.345 \times 10^{-2} J(J+1) - 1.162 \times 10^{-5} [J(J+1)]^2, \quad (1)$$

$$\text{BiD: } Q(J) = 16\,341.018 + 2.858 \times 10^{-2} J(J+1) - 0.285 \times 10^{-5} [J(J+1)]^2.$$

Even at very high resolution ($\sim 6 \times 10^5$) we found no indications of hfs in the lines belonging to the transition $A\ ^1\Sigma - X\ ^1\Sigma$. In the blue region of the spectrum,

$$\sigma_0(\text{BiH}) = 21\,278.39, \quad \sigma_0(\text{BiD}) = 21\,276.25.$$

This enables us to relate the hfs here discussed to the $^1\Pi$ state. It appears from Fig. 1 that the hfs decreases rapidly with increasing J . This behavior may be interpreted according to Hund's case a_β ,³ denoting a firm coupling of the electronic orbitals to the molecular axis while the nuclear spin is more strongly coupled to J . F and J correspond to the total angular momentum of the molecule, F including the nuclear spin of Bi, $I=9/2$. The energy of interaction between the magnetic moment of the Bi nucleus and the molecular rotation may therefore be given by

$$W_{\text{magn}} = hc \times A [F(F+1) - J(J+1) - I(I+1)] / J(J+1), \quad (2)$$

where W_{magn}/hc is to be added to the expressions given in (1).

The observed hfs in both isotopic molecules is very precisely represented by (2) with

$$A = 0.0540 \text{ cm}^{-1},$$

including all permitted components ($2J+1$) in the three lowest states of rotation. For $J > I$, the hfs is not resolved; however, its total width, corresponding to $F=J+I$ and $F=J-I$, decreases regularly according to (2). The hfs in the P and R branches, not shown in Fig. 1, agrees closely with the hfs in the Q branches, although our observations here are not so complete as in the Q branches. It was, however, of interest to confirm this relation as their hfs originates from different spectral terms Π_c and Π_d . It may also be noted that the observed Λ doubling $\gamma J(J+1)$ between these states fulfils the conditions for a state in pure precession:

$$\gamma = 2B^2 J(J+1) / ({}^1\Pi - X\ ^1\Sigma),$$

$$\text{BiH: } \gamma = 0.0200, \quad \text{BiD: } \gamma = 0.00492.$$

Finally, we note from Fig. 1 that the centers of the hfs, $W_{\text{magn}}=0$, for the first lines ($J < 6$) are "uncoupled" from the positions calculated according to (1).

A detailed description of the technique applied in this investigation will be given later.

¹ E. Hulthén and H. Neuhaus, *Nature* **173**, 442 (1954); *Arkiv Fysik* **8**, 343 (1954).

² E. Hulthén, *Nature* **79**, 57 (1932).

³ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

Elementary Theory of the Excitations in Liquid Helium: New Model for Rotons*

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CONSIDERABLE light is thrown on the properties of liquid He³ by a pair-rotator model in which it is assumed that N atoms form $N/2$ pairs.¹ If these pairs have one lowest energy level, three excited levels at about 0.8 calorie per pair-mole, and eight at about 5.4 calories per pair-mole, it is possible to account roughly for the thermodynamic properties at low temperatures.² These energy levels are about correct for a plane rotator moving in a hindering potential of about 12 calories per pair-mole due to the neighboring atoms.³ The level at 0.8 is threefold because it is a spin triplet. The next level should also be a spin triplet, but presumably has a greater multiplicity because of random pairing³ of a given atom with any of its neighbors.

The spin-triplet levels in He³ do not exist in He⁴ because of the lack of spin and the different statistics. The first excited (roton) level in He⁴ would have an excitation of about 11 calories per pair-mole if it had the same hindering potential.⁴ Actually the observed specific heat requires that it have an excitation energy of about 20, but the hindering potential would be expected to be greater than in He³ on account of closer approach of the atoms. It is difficult to estimate how much increase in the zero-point energy of the atoms in the pair making the rotation, in the direction crosswise to the direction of rotation, contributes to the effective hindering potential. If, however, the difference between He⁴ and He³ arises from greater penetration of the rotating He⁴ pairs into the steep part of the potential-energy curve, which begins at about 2.9 Å, we may make an estimate of the difference in the hindering potential. If, for example the distance of approach of each of the atoms of a rotating pair to its neighbor, at the height of the hindering potential, were 2.8 Å in He³, it would, if proportional to the cube root of the molecular density, be about 2.55 Å in He⁴. From the potential-energy curve,⁵ this could result in a fivefold increase in the hindering potential, giving an excitation energy of about 22 calories for a rotating pair in He⁴.

The multiplicity of the excited level of He⁴ appears to be about 18, reckoned on the pair basis. It has already

been pointed out that this might result from the involvement of more than two atoms in a roton.³ We now wish to propose a definite model for He⁴, in which two pairs rotate cooperatively, somewhat as interlocking gears. With this model, the reduced mass μ would be doubled and the parameter q would be doubled for a given hindering potential. The value of $16q+4\alpha$ would, however, increase only about 50%, and when allowance is made for the changed μ , the actual excitation energy would go down from 22 to about 16 calories. However, cooperative motion of this sort would require an increase in the zero-point energy, by the uncertainty principle. (This is the reason the levels of He³ which involve less excitation are free of this effect.) On the other hand, the cooperative action itself might result in some lowering of the hindering potential.

The expected number of pairs of pairs, assuming four nearest neighbors in the liquid, would be $3^2 \times 4N/2$ (the number of nearest neighbor pairs is $4N/2$; each of the atoms in such a pair can connect with any one of the three remaining neighbors, all spatially different, to form a pair of pairs). Dividing by $N/2$, the number of pairs in the cell theory, we obtain an effective multiplicity of 36 per pair. This is twice the observed multiplicity, but it need not be expected that this degeneracy would be fully developed. On the whole, this elementary and pictorial theory gives a surprisingly good account of the experimental results for both He³ and He⁴, both as regards energy and multiplicity of the elementary excitations.

The question now arises, how does this picture fit in with that recently discussed by Feynman and others,⁶ in which the roton is described as a sort of "smoke ring" of helium atoms? A cooperating pair of atoms certainly does resemble a smoke ring in some respects. There is, however, a difference in the method of counting the energy levels. We have used a cell theory, or what might be called a space configuration statistics. On account of the large zero-point energy this obviously involves an approximation. With heavier atoms than helium the approximation would be better, but we might expect that even with helium we would at least get correct orders of magnitude. In the theory of Feynman and the earlier theory of Landau, on the other hand, the multiplicity of levels is taken care of by considering a gas of excitations, and the momentum of these excitations is involved.

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¹ P. J. Price, *Phys. Rev.* **97**, 259 (1955); O. K. Rice, *Phys. Rev.* **97**, 263 (1955); J. de Boer and E. G. D. Cohen, *Physica* **21**, 79 (1955).

² H. N. V. Temperley, *Proc. Phys. Soc. (London)* **A68**, 1136 (1955).

³ O. K. Rice, *Phys. Rev.* **98**, 847 (1955).

⁴ See Fig. 1 of reference 3. (For some of the considerations of this note this figure should be extended to larger values of q .)

⁵ J. L. Yntema and W. G. Schneider, *J. Chem. Phys.* **18**, 646 (1950), Eq. (19).

⁶ R. P. Feynman, *Phys. Rev.* **94**, 262 (1954); R. P. Feynman and M. Cohen, *Progr. Theoret. Phys.* **14**, 261 (1955); C. G. Kuper, *Proc. Roy. Soc. (London)* **A233**, 223 (1955).