to obtain

$$[(n_3+n_4)-(n_5+n_6)]_t$$
$$= [(n_3+n_4)-n_5+n_6)]_0 \exp(-K_{100}t), \qquad (7)$$

where

$$K_{100}(T) = 6P_{60}. \qquad (8)$$

In this case the anisotropy is proportional to $[(n_3+n_4)-(n_5+n_6)]$ so that (7) constitutes a derivation of (1) for series-II experiments. Thus,

$$\frac{K_{110}(T)}{K_{100}(T)} = \frac{2}{3} + \frac{1}{3}\frac{P_{90}}{P_{60}}. \qquad (9)$$

Since P_{90} and P_{60} are both $\geqslant 0$, it follows from (9) that $[K_{110}(T)/K_{100}(T)] \geqslant \frac{2}{3}$. From the data of Fig. 2 we find that $(K_{110}/K_{100}) = 0.65 \pm 0.02$, and is temperature independent, from which we conclude that P_{90} is effectively zero and $P_{60} = (1.0\times10^{13})\exp(-E/kT)$ sec^{-1}, where $E = 0.273$ eV. Thus, the results indicate that V_K reorientation takes place almost exclusively through jumps to a new site at 60° to the original site. The fact that $P_{90} = 0$ indicates that reorientation occurs through one-step jumps in which only one of the two halides constituting the V_K center is changed. (If a migratory motion occurred in each jump the recapture site should be random, with $P_{90} \approx P_{60}$.) We note that in the lattice of V_K sites (midpoint between two adjacent halides), the first *nn* positions to a given V_K site are oriented at 60° to the axis of the reference site; the second *nn* positions are oriented at 90°. The preferred reorientation is therefore to the first *nn* site. It may also be noted that the closest site having the same orientation as the reference site is a fourth *nn* position.

The experiments reported here do not provide information on the total jump frequency of V_K centers, as a jump to a new site of the same orientation (frequency P_0) cannot be observed in anisotropy measurements. However, the quantity $4P_{60}$ must represent a lower limit, as the total jump frequency would be given by $P_0 + P_{90} + 4P_{60} = P_0 + 4P_{60}$. At 100°K, $4P_{60}$ is of order 1 sec^{-1} and, at 110°K, $4P_{60}$ is about 10 sec^{-1}. On the basis of 60° jumps only, the V_K center would be moving several lattice sites per second in this temperature region. It is known[2,3] that V_K centers in KI become thermally unstable (lifetime of order seconds) at about 105-110°K, so that the migration of V_K centers can be accounted for reasonably by 60° jumps only. This argues that P_0 is at most comparable to $4P_{60}$, but is not much greater. It is, of course, possible that $P_0 \ll 4P_{60}$.

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*Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

†Oak Ridge Institute for Nuclear Studies Predoctoral Fellow from the University of Tennessee.

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CHANGE IN THE CRYSTAL STRUCTURE OF SOLID NORMAL HYDROGEN NEAR 1.5°K*

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(Received 1 July 1965)

We have recently observed an effect in the infrared absorption spectrum of solid normal hydrogen which provides evidence that the crystal structure of hydrogen changes in the neighborhood of 1.5°K. The change in the spectrum occurs at the same temperature as the λ anomaly in the specific heat.[1]

The absorption spectra were obtained using a monochromator equipped with an optical cryostat which has previously been described.[2] To minimize heating of the solid hydrogen sample, the monochromator was placed between the infrared source and the cryostat, the infrared detector being placed after the cryostat; the heat input to the hydrogen crystal from the monochromator was less than that generated by slow conversion of the ortho to the para species.[3] The temperature difference between the crystal and the liquid-helium bath is estimated to be less than 0.001°K.

The fundamental absorption band of solid normal H_2 is shown at a temperature of 1.9°K in Fig. 1(a) and at 1.3°K in Fig. 1(b). The features labeled $S_1(0)$ and $S_1(1)$ have practically disappeared in the low-temperature spectrum; the Q_Q feature has split; and, in addition, the Q_R

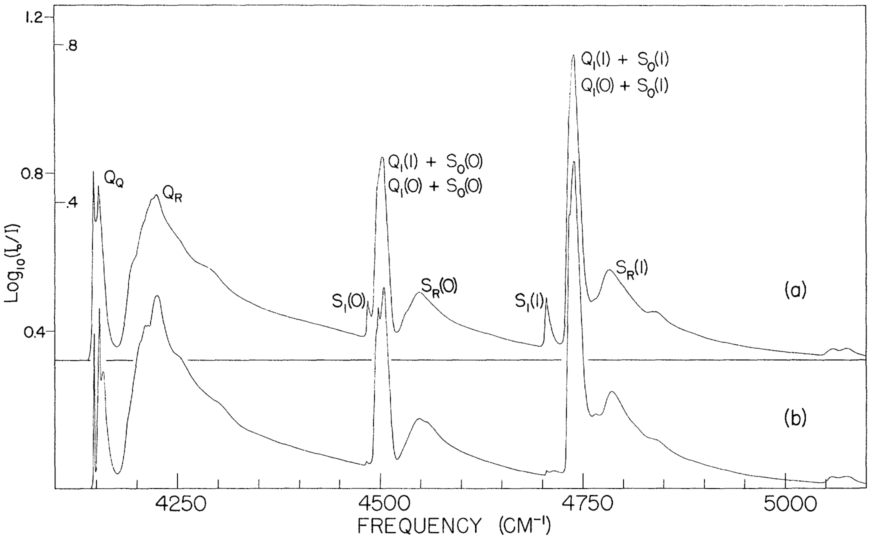

FIG. 1. The spectrum of solid normal hydrogen at 1.9°K [curve (a)] and 1.3°K [curve (b)].

and S_R branches have changed shape. This change in the spectrum takes place over a small temperature range. The spectra may be characterized by the area of the $S_1(1)$ line, and this quantity is plotted as a function of the temperature in Fig. 2. As the crystal is cooled a temperature is reached (~1.5°K for normal H_2) at which the intensity of the $S_1(1)$ line begins to fall, and it drops nearly to zero if the temperature is lowered about 0.1°K; the spectrum undergoes no further change to the lowest temperature reached, 1.2°K. If the crystal is now warmed the $S_1(1)$ line remains weak until the temperature has been raised about 0.2°K above the first transition temperature, when the intensity of the line returns. The transition temperatures on cooling and heating are strongly dependent on the ortho-para ratio; several different cases are included in Fig. 2. The transition temperature[4] as a function of ortho-para ratio is shown in Fig. 3. For comparison, the temperatures of the specific-heat anomaly[1] and the anomaly in the nuclear-magnetic-resonance spectrum[5,6] are also shown. The transition temperatures of the different phenomena

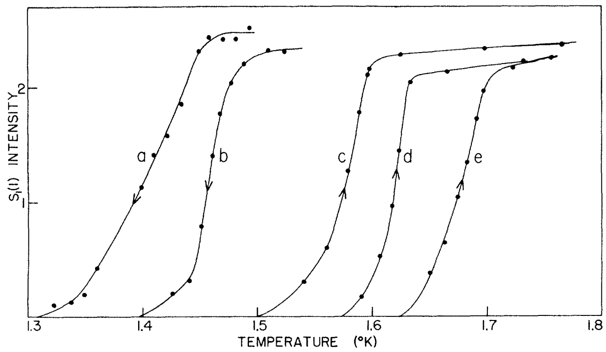

FIG. 2. The area of the $S_1(1)$ line as a function of temperature. The arrows denote the direction of temperature change. The ortho concentration is curve a, 73 %; curve b, 74 %; curve c, 72.2 %; curve d, 73.5 %; and curve e, 74 %.

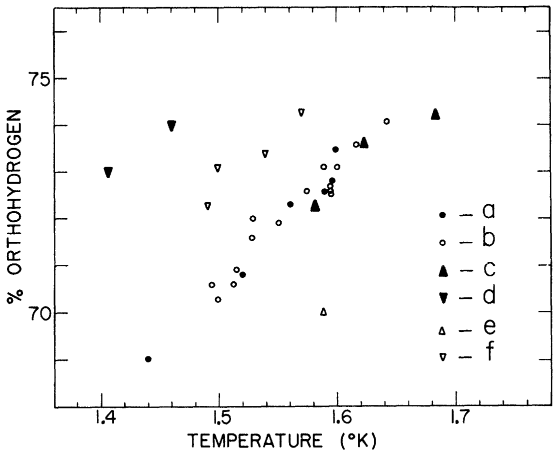

FIG. 3. The transition temperature as a function of orthohydrogen concentration as observed in different experiments. The temperature of the specific-heat anomaly measured by Hill and Ricketson[6] and by Ahlers and Orttung[1] is shown by points (a) and (b), respectively. The transition observed in the present work is shown by points (c) (temperature rising) and (d) (temperature falling). The nmr anomaly is shown by points (e) (temperature rising) and (f) (temperature falling) (see Smith and Housley[5]).

do not agree exactly, but they have the same dependence on ortho concentration. Furthermore, the hysteresis effect observed here is very similar to that observed in the nmr experiments.

The spectrum of solid H_2 has been analyzed by Gush et al.[2] and by Van Kranendonk.[7] Three types of transition may be distinguished: (1) transitions in which a single molecule changes its state; for example, $v=0\rightarrow v=1$; $J=0\rightarrow J=2$ [$S_1(0)$ feature], or $v=0\rightarrow v=1$; $\Delta J=0$ (Q_Q feature), where v is the vibrational quantum number and J is the rotational quantum number; (2) transitions in which two molecules change their state; for example, $v_1=0\rightarrow v_1=1$; $J_1=0\rightarrow J_1=0$, $v_2=0\rightarrow v_2=0$; $J_2=0\rightarrow J_2=2$, which gives rise to the $Q_1(0)+S_0(0)$ feature; (3) transitions in which a molecular excitation is accompanied by the creation of a phonon in the crystal; these are responsible for the Q_R and S_R phonon branches.

The $S_1(0)$ and $S_1(1)$ lines arise from the quadrupolar induction effect. The intensity is proportional to the square of the sum of the dipole moments induced by the quadrupole field of the absorbing molecule in all neighboring molecules. In parahydrogen this sum vanished if the central molecule is at a center of inversion symmetry. The fact that the $S_1(0)$ line is observed in parahydrogen is proof that the parahydrogen crystal does not possess inversion symmetry.[8] The calculation by Van Kranendonk[7] of the intensity of the $S_1(0)$ feature in parahydrogen can be extended to the case in which the absorbing paramolecule is surrounded by orthomolecules instead of paramolecules. The intensity for normal H_2 is the same as for para-H_2 except for a small contribution arising from the anisotropy of the polarizability of the orthomolecules. If the crystal structure of normal H_2 is assumed to be hexagonal close-packed, and if the orthomolecules are assumed to be randomly oriented, then the intensity of the $S_1(0)$ line per paramolecule in normal H_2 should be about 15% greater than the same feature in para-H_2. In fact, this is what is observed: For normal H_2 at 1.9°K, $\tilde{\alpha}[S_1(0)]=4\times10^{-15}$ cm^3 sec^{-1}, and for para-H_2, $\tilde{\alpha}[S_1(0)]=3.3\times10^{-15}$ cm^3 sec^{-1}.[9,10] The calculated value of $\tilde{\alpha}$ in para-H_2 equals 3×10^{-15} cm^3 sec^{-1}.[7] If one assumes a crystal structure for normal H_2 which possesses inversion symmetry, the major contribution to the intensity of the $S_1(0)$ line vanishes, leaving only the contribution arising from the anisotropy of the polarizability, which is much too small to account for the observed line in the solid at 1.9°K; we conclude that at this temperature the crystal does not have a center of inversion. However, the sudden drop in intensity of both $S_1(0)$ and $S_1(1)$ features when the crystal is cooled can be readily accounted for by a change in the crystal structure to one possessing inversion symmetry. The weak features of the original lines remaining in place owe their intensity to the anisotropic terms discussed above; they are double transitions in which, for example, a paramolecule makes the $S_1(0)$ transition, and a neighboring orthomolecule changes its m state, where m is the magnetic quantum number.

The conclusion that a phase change has taken place is substantiated by two other observations. Firstly, the phonon branches Q_R and S_R in the low-temperature spectrum have a noticeably different shape. One would naturally expect a different lattice-vibration spectrum to be associated with a different lattice structure. Secondly, there is a drop of 25% in the integrated absorption coefficient of the Q_Q component; if a phase change takes place, a loss of intensity of this order is expected on the basis of the theory of this band as developed by Sears and Van Kranendonk.[11]

The phase transition presumably arises because of an ordering of the orthomolecules which have a quadrupole moment; the quadrupolar energy is apparently less on a crystal structure with inversion symmetry. The ground state of orthohydrogen has been investigated assuming a hexagonal close-packed structure[12,13]; it would be of interest to extend these calculations to other crystal structures.

It is a pleasure to acknowledge helpful discussions with Dr. J. Van Kranendonk.

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*This work was supported by a grant from the National Research Council of Canada.

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[3] At a temperature of 1.9°K only the two lowest rotational states of hydrogen are appreciably populated. In normal H_2 75% of the molecules are in the state $J=1$ (ortho species), and 25% are in the state $J=0$ (para species).

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