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Calcium Hydride and Deuteride Studied by Neutron Diffraction and NMR

A. F. ANDRESEN

Institutt for Atomenergi, P.O.B. 40, 2007 Kjeller, Norway

A. J. MAELAND

Allied Chemical, Morristown, N.J.

AND D. SLOTFELDT-ELLINGSEN

Sentralinstitutt for Industriell Forskning, Oslo 3, Norway

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The structure of CaD_2 has been redetermined by neutron diffraction and the structure has been confirmed by NMR measurements. However, the interpretation of the NMR measurements is not easy. The unsymmetrical position of the hydrogen (deuterium) atoms and the large range of interatomic distances lead to complicated spectra. Since the spectra for both the hydride and the deuteride seem to be determined mainly by dipolar interactions, one can conclude that the electric field gradient at the D sites must be very small. Line narrowing above 440°K is ascribed to proton diffusion with an activation enthalpy of 17.4 kcal/mol.

Introduction

The crystal structure of calcium hydride was first studied in 1935 by Zintl and Harder (*1*) who found the space group to be *Pnma* and determined the metal atom positions (Table I). From X-ray data they could not determine the hydrogen positions, but assumed these atoms to occupy two fourfold positions 4(*c*) with parameters as given in Table I. A neutron diffraction investigation carried out in 1961 by Bergsma and Loopstra (*2*) led to essentially different hydrogen positions (Table I). This determination was carried out on poorly resolved diagrams obtained at the low flux reactor JEEP I (central flux 2×10^{12} N/cm^2 sec) and had to rely partly on geometrical considerations. Therefore, a high accuracy could not be claimed, and calculations which we recently carried out based on these parameters did not lead to values for the second moment in reasonable agreement with those obtained from NMR measurements.

We therefore decided to reinvestigate CaD_2 with neutron diffraction, taking advantage of the increased flux and resolution now available. Also an increased accuracy in the determination of the parameters is

TABLE I

ATOMIC POSITIONS IN CaH_2: SPACE GROUP *Pnma*, 4 UNITS CaH_2 pr. CELL

	Ca		H_I		H_{II}	
	x	z	x	z	x	z
Zintl and Harder	0.260	0.110	0.260	0.430	0.996	0.758
Bergsma and Loopstra	0.260	0.110	0.375	0.435	0.000	0.660

now possible through the application of the least-squares profile refinement program worked out by Rietveld (*3*). At the same time we wanted to carry out a more detailed examination of this compound by NMR to obtain more information about the bonding of the protons and the proton–proton, proton–lattice interaction.

Experimental

The deuteride was prepared from calcium metal obtained from Research Organic/Inorganic Chemical Corp. of Sun Valley, California which contained a minimum of 99% Ca according to the suppliers. The calcium was cut under oil in an argon-filled dry box, and after rinsing several times in anhydrous ether, it was put into a stainless steel boat which was inserted into the reaction tube. This was a pipe of stainless steel fitted with a thermocouple well at one end and a flange attachment at the other. The mate to this flange was attached via a Kovar seal to a stopcock equipped with a ball joint for connection to a vacuum line. The assembly was removed from the dry box, connected to the vacuum line, evacuated, and degassed at 250–300°C to 10^{-5} mm Hg. After cooling to room temperature, 99.5% pure deuterium gas was admitted to the system. The sample was then heated to 800°C, held at this temperature for several hours, followed by slow cooling to room temperature. The composition of the sample, $CaD_{2.00\pm0.03}$, was calculated from the change in pressure and the known volume of the system. The product was ground to a fine powder under an argon atmosphere, and then packed and sealed in a vanadium cylinder for the neutron diffraction measurements. Calcium hydride was prepared in a similar way using ultrapure hydrogen of stated purity 99.999%. The composition of the product was $CaH_{1.96\pm0.03}$.

Neutron diffraction measurements were carried out at the JEEP II reactor, Kjeller, using neutrons of wavelength 1.873 Å obtained by reflection from the (111) plane of a squashed germanium monochromator crystal. The data, obtained by step-scanning with steps of 0.1°, was treated by the least-squares profile refinement program of Rietveld (*3*).

The NMR measurements were carried out at the Central Institute for Industrial Research, Oslo. The proton and deuteron magnetic resonance (PMR and DMR) derivative absorption signals were recorded using a Varian (Model V-4200) cw spectrometer and a 12-in. electromagnet system with a Fieldial control. The operating frequencies were $\omega_0/2\pi = 60.0$ and 7.9 MHz for proton and deuteron resonance, respectively. The spin–lattice relaxation times were measured using a home-made pulse spectrometer. The pulse sequence was 90°-τ-90°-τ- and the resonance frequency was 10.0 MHz.

Results and Discussion

Neutron Diffraction

The neutron diffraction pattern of the CaD_2-sample is shown in Fig. 1. The squares represent the observed points. The data, collected on paper tape, were used as input to the least-squares profile refinement program of Rietveld. Starting parameters were the atomic position parameters given by Bergsma and Loopstra (Table I) and unit cell dimensions obtained from a separate least-squares program based on the peak positions. The following parameters were refined: the position parameters x and z for the calcium and deuterium atoms, the individual temperature factors, the cell constants, the scale factor, and three half-width parameters. The resulting parameters, temperature factors, and cell constants are given in Table II together with their standard

TABLE II

PARAMETERS AND LATTICE CONSTANTS FOR CaD_2: RESULTS OF LEAST-SQUARES PROFILE REFINEMENT

	x	z	B
Ca	0.2378(13)	0.1071(8)	0.19(19)
D_I	0.3573(6)	0.4269(7)	1.55(28)
D_{II}	0.9737(9)	0.6766(5)	1.55(28)
	$a = 5.925(1)$	$b = 3.581(1)$	$c = 6.776(1)$
	$R = 3.71\%$		

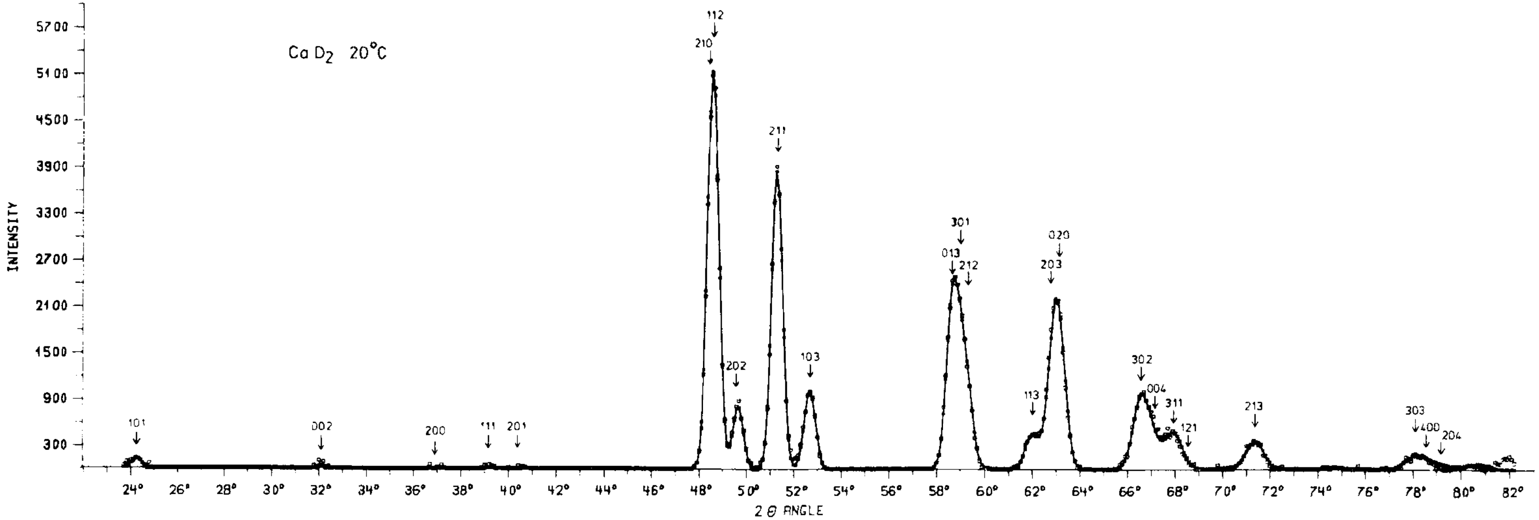

FIG. 1. Neutron diffraction pattern of $CaD_{2.00}$. $\lambda = 1.873$ Å. □, observed points; x, calculated profile connected with fully drawn line.

deviations. The final R factor for the intensities was 3.71% and for the profile was 8.40%. In Fig. 1 we have also plotted the calculated profile (crosses) connected with a fully drawn line. The agreement with the observed profile (squares) is seen to be satisfactory for all the peaks.

In the calcium deuteride structure (Fig. 2) the Ca ions are surrounded by nine D ions at distances ranging from 2.240 to 2.632 Å. Of the D ions, the D_I ions are surrounded in a closely tetrahedral configuration by four Ca ions at distances between 2.240 and 2.279 Å, and by eight D ions at distances ranging from 2.655 to 2.833 Å. The D_{II} ions are surrounded by five Ca ions at distances ranging from 2.376 to 2.632 Å and 10 D ions at distances between 2.662 and 3.125 Å. The shortest D–D distance is thus 2.655 Å.

Because of the large change in the PMR spectra (Fig. 3) observed on heating the sample from 298 to 533°K, and since we expect the deuteride to behave in the same way, neutron diffraction diagrams were run at several different temperatures between 298 and 673°K to look for structural changes. Except for uniform increases in the unit cell dimensions with temperature, no significant change in the diffraction pattern was observed. A profile refinement calculation carried out on data obtained at 573°K revealed only slight changes in the atomic position parameters. The largest changes were observed for the deuterium atoms in the D_I positions ($\Delta x = -0.007$ Å and $\Delta z = -0.006$ Å). As a result of these changes, the distances between a Ca ion and its surrounding nine D ions now range between 2.226 and 2.655 Å. The D_I ions are surrounded by a tetrahedron of Ca ions at distances ranging from 2.226 to 2.347 Å and the D_{II} ions by five Ca ions at distances from 2.396 to 2.655 Å. Thus, except for a general increase in the interionic distances, there are no significant changes in either the distances or angles which can explain the large change in the PMR spectra observed. This must rather be ascribed to the increase in hydrogen diffusion with temperature, as discussed below.

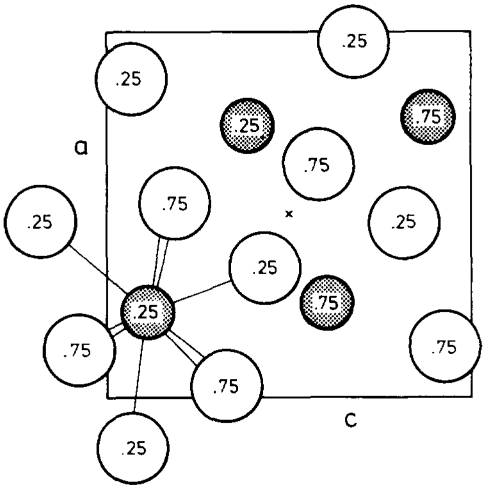

FIG. 2. Projection of the unit cell of CaH_2 on the b-plane; numbers give the height above the plane. Metal atoms are shaded.

Nuclear Magnetic Resonance

The PMR signal was recorded in the temperature range from 145 to 680°K. The shape of the spectra changes with temperature as shown in Fig. 3; the changes are temperature reversible. Below room temperature, the resonance spectrum has a complicated shape, which does not change with temperature. In the region from about 300 to 370°K, however, this shape develops into a spectrum with pronounced fine structure. Qualitatively, it resembles the spectrum of a two-spin system. In a basically many-spin system like CaH_2, such resonance shapes are difficult to interpret. Experimental conditions, like the saturation level or the modulation field amplitude, did not influence the spectra in any unexpected way, and the shape, therefore, seems to be caused by the crystal structure.

At higher temperatures the resonance narrows, and the fine structure disappears. The shape of the resonance in this region is intermediate between a Gaussian and a Lorentzian, as usually observed in hydrides in this region. At still higher temperatures (>600°K) the shape becomes Lorentzian. Below 440°K the peak-to-peak linewidth is constant, $\Delta B_L = 9.4$ G. Between 440 and 545°K it decreases, and above 545°K it is again constant, $\Delta B_H = 1.0$ G (Fig. 4).

Some information about the crystal structure can be obtained from the second moment,

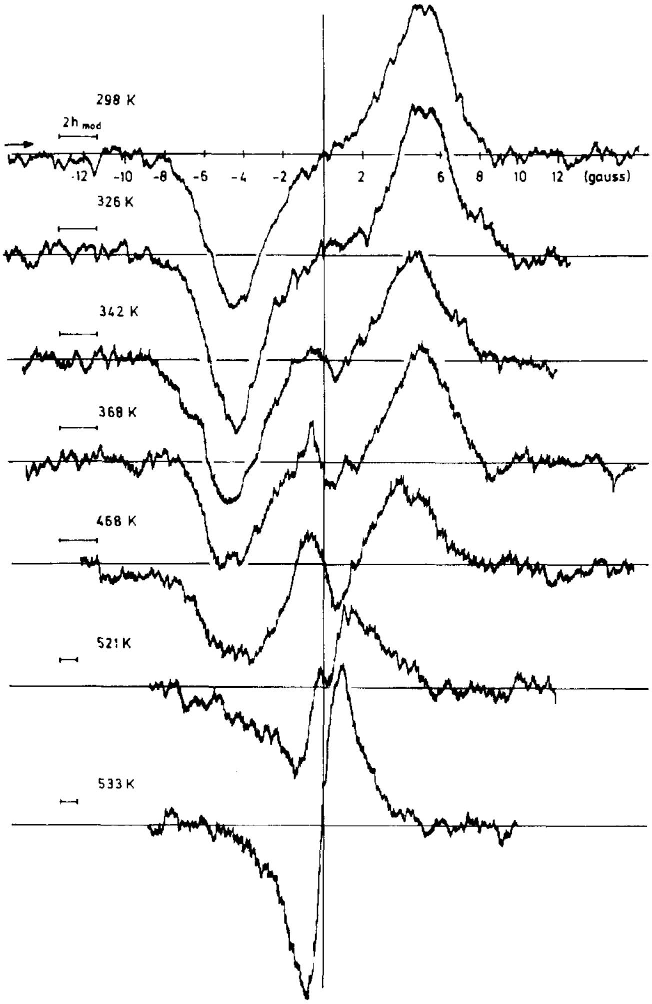

FIG. 3. PMR spectra of $CaH_{1.96}$. The bars indicate the peak-to-peak modulation field amplitudes used.

M_2, of the absorption signal. M_2 is defined as

$$M_2 \equiv \int_{-\infty}^{+\infty} (B - B_0)^2 \cdot g(B) \cdot dB \Big/ \int_{-\infty}^{+\infty} g(B) \cdot dB, \tag{1}$$

where $g(B)$ is the shape function of the absorption signal, $B_0 = \omega_0/\gamma_H$ is the static, magnetic field at the center of the resonance, and γ_H is the proton magnetogyric ratio. M_2 was calculated by numerical integrations of the experimental spectra. Spectra with too low signal-to-noise ratios were omitted. The results are included in Fig. 4. The room temperature second moment is about 10% smaller than the average second moment of the spectra which has a pronounced fine structure. This difference is slightly larger than the uncertainty in these data, so that a modest increase in the second moment may be associated with the appearance of the fine structure. The reason why the rather marked changes in shape eventually do not result in larger changes in M_2 is that the wings of the spectra, which represent the major contribution to M_2, are practically unaltered.

Theoretically, the second moment is a measure of the strength of the magnetic dipole interaction between protons. In the case of a "rigid lattice" we have *(4)*:

$$M_2 = \tfrac{3}{10}\gamma_H^2 \hbar^2 \Big(\sum_{j \neq 1} r_{1j}^{-6} + \sum_{j \neq 2} r_{2j}^{-6} \Big) \tag{2}$$

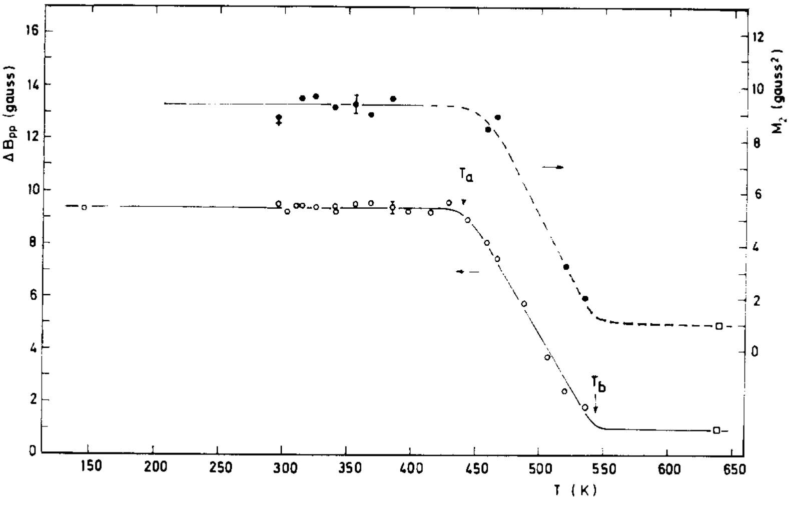

FIG. 4. The temperature dependence of the PMR second moment (●) and peak-to-peak line width (○) of $CaH_{1.96}$. □, calculated from the free induction decay, Lorentzian lineshape, +, calculated from Eq. (2).

where r_{ij} is the distance between proton i and j. Proton $i = 1$ is in H_I position, and proton $i = 2$ in H_{II}. The sums go over all protons in the crystal. We have calculated M_2 in this way using the crystal structure and dimension parameters obtained from our neutron diffraction investigation on CaD_2 (Table II). Isotope differences were neglected. We found $M_2 = 8.6\ G^2$, which is only 7% lower than the observed average value of $9.3\ G^2$, and close to the room temperature value, $8.8\ G^2$. The agreement is satisfactory and serves to confirm the crystal structure.

The proton spin-lattice relaxation time, T_1, was measured between 490 and 860°K (Fig. 5). Below these temperatures the free induction decay is too short (ΔB too broad) to be observed. T_1 decreases with increasing temperature until a minimum, $T_1(\min) = 0.017$ sec is reached at about 818°K. The temperature dependence of T_1 is caused by hydrogen diffusion, and is discussed below.

While the shapes of the PMR spectra are determined by the *dipolar* interaction between protons, the shapes of the DMR spectra are expected to depend on the interaction between the deuteron electric *quadrupole* moment and the electric field gradient in the deuteron lattice sites. In CaD_2 these field gradients are noncubic and nonaxial, and one would expect the DMR spectrum to consist of two superimposed, quadrupole broadened signals with nonzero asymmetry parameters. Below about 500°K, the cw DMR spectrum av CaD_2 is very difficult to detect because of severe saturation effects even when using the lowest possible radiofrequency field amplitudes. The spectrum seems to be nearly Gaussian, with a peak-to-peak linewidth of about 2 G. If the signal were completely determined by *dipolar* interactions between dueterons, we would expect the DMR linewidth to be less than the PMR linewidth by a factor of about $\frac{1}{3}$. The PMR width is 9.4 G and we would therefore expect a dipolar linewidth of about 3 G in the DMR case—which is close to what we observe.

Also the deuteron spin-lattice relaxation time seems to be determined by the *dipolar* interaction. T_1 in CaD_2 is too long to be measured, which is in agreement with the fact that T_1 for deuterons should be about 500 times longer than for protons, if the relaxation mechanism is the dipolar interaction.

In order to explain the small quadrupole coupling constant in CaD_2, we have calculated the electrostatic field gradients at the deuteron sites. The crystal was assumed to consist of point charges, and values of $+2e$

FIG. 5. The temperature dependence of the spin–lattice relaxation time, T_1. ●, observed points; —, best fit to data; ■, observed point for T_2; □, calculated point for T_2 based on ΔB_L.

and $-e$ were used for Ca^{2+} and D^- ions, respectively. We found

$$\begin{array}{ll}\eta = 0.28 & \\ \nu_Q \approx 1.4\text{ kHz (2.2 G)} & \text{D}_\text{I}\text{—positions}\end{array}$$

$$\begin{array}{ll}\eta = 0.36 & \\ \nu_Q \approx 0.8\text{ kHz (1.3 G)} & \text{D}_\text{II}\text{—positions}\end{array}$$

Here $\nu_Q = 3e^2 Q|V_{zz}(1-\gamma_\infty)|/2h$ is the quadrupole splitting frequency and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter (*5*). $Q = 2.77 \cdot 10^{-31}\,\text{m}^2$ is the deuteron quadrupole moment, while $\gamma_\infty \approx 1.1$ (*5*) is the shielding parameter, and V_{ii} are the calculated components of the electrostatic field gradient.

The calculated quadrupole coupling constants are small and in agreement with the observed DMR lineshape and relaxation time.

Hydrogen Diffusion

In a classical, harmonic approximation, the jump rate of the hydrogen atom can be written:

$$\nu = \tau^{-1} = \nu_0 \exp(\Delta S/R) \exp(-\Delta H/(RT)), \tag{3}$$

where τ is the average time between each diffusional jump, ν_0 is a frequency factor, ΔS is the activation entropy, and ΔH is the activation enthalpy of the diffusion process. In hydrides, τ can be set equal to the correlation time, τ_c, of the proton magnetic dipole interaction. We can find τ_c, and thereby τ, by several different NMR techniques (*6*).

From the temperature dependence of ΔB in the region where the narrowing occurs, both ΔH and the "preexponential factor," $P \equiv \nu_0 \cdot \exp(\Delta S/R)$, can be calculated. In this region the jump frequency is related to the linewidth in the following way (*7*):

$$\nu = \alpha \cdot \gamma_H \cdot (\Delta B - \Delta B_H) \cdot [\tan(\pi/2 \cdot (\Delta B - \Delta B_H)^2/(\Delta B_L - \Delta B_H)^2]^{-1}. \tag{4}$$

α is a numerical factor of order 1, which depends on the shape of the resonance signal. Strictly this relation is only valid if the signal is Gaussian at low ($<T_a$) temperatures. This is not the case in CaH_2, and a systematic error in ν and P is therefore possible. If α changes with temperature, an additional error in both ν, P, and ΔH may occur. Nevertheless, we expect Eq. (4) to be accurate enough to give a physical meaningful estimate of the diffusion rate. The results, using $\alpha\gamma_H = 10^4$ Hz/G (α value as for Gaussian shape), $\Delta B_L = 9.4$ G and $\Delta B_H = 1.0$ G, are shown in Fig. 6.

The diffusion rate can be obtained more accurately from the spin–lattice relaxation time measurements. If we assume the motion to be isotropic, we have (*8*):

$$T_1^{-1} = C \cdot [\tau/(1 + \omega_0^2 \cdot \tau^2) + 4\tau/(1 + 4 \cdot \omega_0^2 \cdot \tau^2)], \tag{5}$$

where C is a constant which depends on the crystal structure. The best fit of this relation to the experimental T_1 data is obtained using

$$C = 2.55 \cdot 10^9\ \text{sec}^{-2}$$

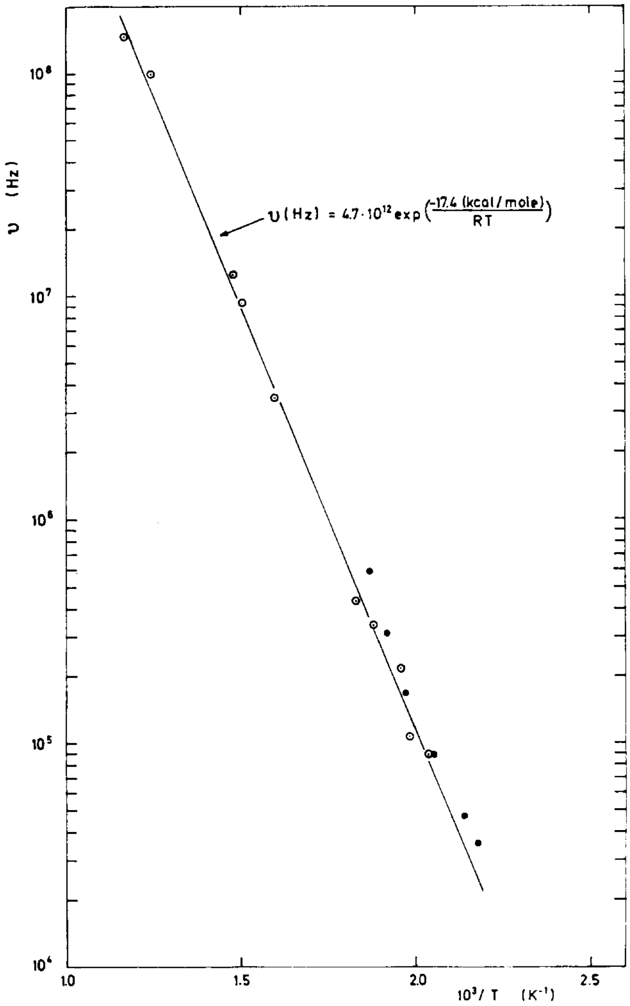

FIG. 6. The temperature dependence of the hydrogen diffusion rate in $CaH_{1.96}$. ●, From line width measurements and Eq. (4); ○, from T_1 measurements and Eq. (5); —, best fit to T_1 data.

and

$$\nu(\text{Hz}) = 4.2\cdot10^{12}\cdot\exp\,[-17.4\,(\text{kcal/mol})/(RT)].$$

These results (Fig. 6) are in good agreement with the ν values calculated from the linewidth measurements.

C is related to the second moment of the absorption signal (9):

$$C = 2/3\cdot\gamma_H^2\cdot(M_{2L} - M_{2H}). \qquad (6)$$

Using $M_{2L} = 9.3$ G^2 and $M_{2H} = 1.0$ G^2, we find $C = 3.9\cdot10^9$ $\sec^{-2}$, in reasonable agreement with the experimental value.

The high temperature linewidth $\Delta B_H =$ 1 G is rather broad. From the T_1 measurements, one would expect ΔB to reach its high-temperature plateau at a higher temperature, and having a lower value of ΔB_H. This indicates that the motion responsible for the observed temperature dependence of both T_1 and ΔB does not average the dipolar interaction completely. Therefore, it may be that this motion does not consist of random, uncorrelated jumps of protons between the available lattice positions, but rather of jumps between certain sets of positions. We believe that this complicated motion is reflected in the unusual shape of PMR spectra. At still higher temperatures one would expect a random jumping between all hydrogen lattice sites to be the dominant motion, causing ΔB to decrease even further (as indicated in Fig. 4).

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