

Motion of negative charges and vacancies in parahydrogen

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The diffusion coefficient of negative charges, D_- , falls off monotonically in hcp p - H_2 crystals over the temperature interval 13.6–5.8 K. At $T > 10$ K, the value of D_- is close to the self-diffusion coefficient D_p in the region of a thermally activated motion of the molecules. The typical activation energies for charges, Δ_- , and for molecules, Δ_s , are nearly twice as large as the known vacancy formation energy E_v . Below 8 K, Δ_- is essentially the same as E_v . This result confirms an earlier suggestion [A. A. Levchenko and L. P. Mezhov-Deglin, Zh. Eksp. Teor. Fiz. **98**, 349 (1990) [Sov. Phys. JETP **71**, 196 (1990)]] that the motion of negative charges in p - H_2 is controlled by a vacancy mechanism. It also supports the earlier theoretical suggestion [C. Ebner and C. C. Sung, Phys. Rev. **B 5**, 2625 (1972)] that the vacancy diffusion mechanism changes from a classical thermally activated mechanism to a quantum-mechanical tunneling as the temperature is lowered.

In solid parahydrogen, the diffusion coefficient for negative charges, D_- , is close to the diffusion coefficient of the orthomolecules, 2D_s , at temperatures above 10 K, as our earlier experiments have shown.¹ The characteristic activation energies for charges, Δ_- , and molecules, Δ_s , are roughly twice as large as the vacancy formation energy E_v in the literature.³ In other words, a classical vacancy mechanism of thermally activated diffusion is playing a leading role in each case. If a molecule is to trade places with a vacancy which has appeared in a neighboring site of the crystal lattice, a potential barrier of height E_b must be surmounted. This height is comparable to the vacancy formation energy.

Below 10 K, the temperature dependence $D_-(T)$, plotted in the coordinates $\log D_- = f(1/T)$, deviated from the straight line $D_- \sim \exp(-\Delta/T)$ for some of the samples studied in Ref. 1. This change may have been due to a change in the properties of vacancies, or it may have been due to a change in the predominant charge diffusion mechanism. It was not possible to study the behavior $D_-(T)$ over a broad temperature range below 10 K previously because of the exponential increase in the time of arrival of the charged-particle front at the collector with decreasing temperature and the strong trapping of moving charges by defects in the interior of the sample.

Refinements of the experimental procedure of Ref. 1 have made it possible to expand the range of the transit-time measurements to 4×10^4 s. The sample, with grounded electrodes, was subjected to a high-temperature annealing before each measurement at $T < 10$ K in order to reduce the effect of the trapped space charge on the time of arrival of the front of the charged particles moving from the source of the charges to the collector. It thus became possible to study the $D_-(T)$ dependence over the broad temperature range from the triple point to 5.8 K. The diffusion coefficient

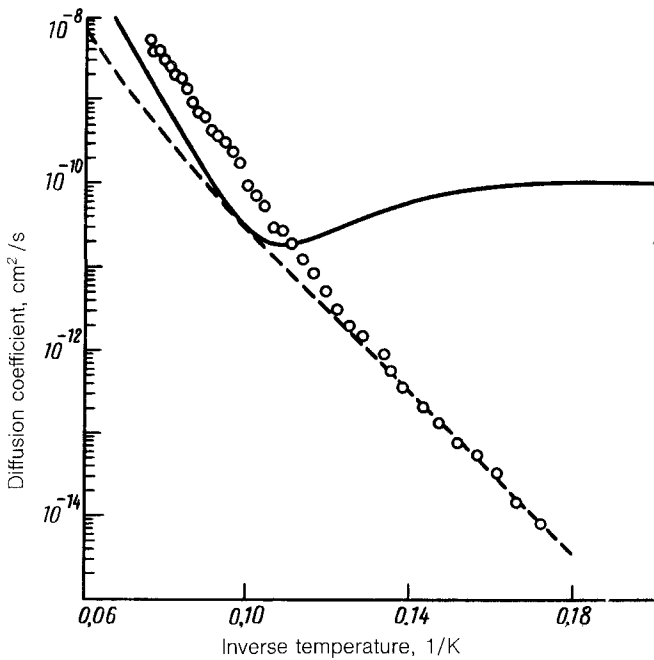


FIG. 1. Defect diffusion coefficient versus the inverse temperature. Open circles—Negative charges (sample 91); dashed line—theoretical behavior of the diffusion coefficient of molecules which are interacting with vacancies;³ solid line—experimental behavior of the diffusion coefficient of HD molecules in p -H₂ constructed from the data of Ref. 5.

for the positive charges, D_+ , could not be measured beyond 9 K, since the value of D_+ is much lower than D_- in p -H₂ crystals.

Figure 1 shows the temperature dependence of the diffusion coefficient for negative charges in one of the better samples (sample 91 was grown at a pressure of 1.5 atm from liquid parahydrogen). The error of the $D_-(T)$ measurements does not exceed the size of the points in this figure. The slopes of the $D_-(T)$ curves may differ from sample to sample.¹ One reason for this variation is obvious: the anisotropy of the properties of hcp crystals. An additional anisotropy may be caused in the case of the motion of a charged defect, by differences between the symmetry of the charge and the symmetry of the surrounding crystal lattice.⁴ In low-quality samples, the measured transit time may increase because of a buildup of trapped charge in the interior. The effect would be to reduce the value of D_- from that for a high-quality sample. We will accordingly restrict the discussion in the present letter to the $D_-(T)$ behavior for the best sample, with the highest negative-charge mobility at low temperatures.

The solid line here shows a temperature dependence of the diffusion coefficient $D_i(T)$ of HD impurity molecules in parahydrogen samples which we calculated from a curve of the longitudinal relaxation time of HD molecules given in Ref. 5. Above 10 K, the values of D_- and D_i are approximately the same. Below 10 K, the temperature dependence $D_-(T)$ is fundamentally different from $D_i(T)$. As was mentioned in Ref.

TABLE I.

Reference	D_c $10^{-3}\text{cm}^2/\text{s}$	$E_v + E_b$ K	D_q $10^{-8}\text{cm}^2/\text{s}$	E_v K
Present study	1.8	168 ± 5	23	100 ± 5
Ref. 3	0.6	197	200	112
Ref. 5	4.9	198 ± 6	9.8	91 ± 6

5, the deviation of D_i from an activation dependence with decreasing temperature may be due to a change in the diffusion mechanism for the HD molecules: from a classical thermally activated diffusion (molecules and vacancies trade places) to a quantum-mechanical tunneling diffusion of HD molecules in the crystal.

The dashed line shows the $1/T$ dependence of the self-diffusion coefficient predicted by the theory of Ref. 3. That curve was calculated under the assumption that the motion of the molecules is controlled by vacancies. Both a classical thermally activated diffusion and a quantum tunneling of vacancies were taken into account. We see that below 8 K this curve essentially coincides with the experimental $D_-(T)$ curve.

It is thus natural to suggest that the motion of the charges is controlled over the entire temperature interval 13.6–5.8 K by the interaction of the charges with vacancies, i.e., that $D_-(T)$ can be described by an expression $D_- = D_c \exp[-(E_v + E_b)/T] + D_q \exp[-E_v/T]$. This expression was used in Refs. 3 and 5 to explain the vacancy diffusion of molecules in solid hydrogen. The parameter values found through these calculations are listed in Table I. Also shown here are the activation energies for the molecules in the region of a thermally activated diffusion and the vacancy formation energies E_v , taken from Refs. 3 and 5. This table furthermore gives the coefficients of the exponential function D_c and D_q corresponding to a classical thermally activated motion and to a quantum tunneling of vacancies.

We see from this table that the parameter values describing the temperature dependence $D_-(T)$ agree with the theory of Ref. 3 and the NMR data of Ref. 5.

In summary, this comparison of measurements of the diffusion coefficient for negative charges with the results of NMR measurements^{2,5} and with theoretical predictions of the properties of vacancies in hydrogen³ confirms our suggestion that the charges move by a vacancy mechanism in $p\text{-H}_2$ crystals. It also confirms the theoretical suggestion that the primary mechanism for vacancy diffusion at low temperatures (below 8 K, according to our data) is a quantum tunneling.

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¹ A. A. Levchenko and L. P. Mezhev-Deglin, Zh. Eksp. Teor. Fiz. **98**, 349 (1990) [Sov. Phys. JETP **71**, 196 (1990)].

² Handbook on the Properties of Condensed Phases of Hydrogen and Oxygen, Naukova Dumka, Kiev, 1984.

³ C. Ebner and C. C. Sung, *Phys. Rev. B* **5**, 2625 (1972).

⁴ A. F. Andreev and A. D. Savishchev, *Zh. Eksp. Teor. Fiz.* **96**, 1109 (1989) [*Sov. Phys. JETP* **69**, 630 (1989)].

⁵ D. Zhou, M. Rall, J. P. Brison, and N. S. Sullivan, *Phys. Rev. B* **42**, 1929 (1990).

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