Temperature dependence of quantum diffusion of H atoms in solid H_2 in the temperature range 1.35 K$\leqslant T \leqslant$4.2 K

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The temperature dependence of quantum diffusion of hydrogen atoms in solid H_2 in the range 1.35 K$\leqslant T \leqslant$4.2 K is determined experimentally. It is found that the diffusion coefficient depends linearly on temperature, indicating the existence of a new type of quantum diffusion if there is a large displacement of levels.

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The process of recombination of hydrogen atoms in solid H_2 proceeds through two successive stages: diffusion approach of atoms and recombination. The diffusion stage is much slower than the recombination stage, so that the temperature dependence of the recombination rate constant $K(T)$ is analogous to the temperature dependence of the diffusion coefficient $D(T)$.

The dependence $K(T)$ for H atoms in H_2 was first studied in Ref. 1 using the EPR method in the three centimeter range ($B \cong 0.3$ T). It was shown that for $T \gtrsim 4.7$ K $K(T) \sim \exp(-E_a/T)$, where $E_a = 107 \pm 10$ K. It is natural to associate such a dependence with classical diffusion with activation energy E_a. It was found that for $T \lesssim 4.2$ K the dependence $K(T)$ has a completely different nature, which corresponds to a very small drop in K with decreasing T. Such a dependence in the temperature range studied (low temperatures) could be due only to quantum diffusion processes. However, the law governing the temperature change in K, which is important for understanding the nature of the phenomenon, was not determined.

In this work, we undertook a quantitative investigation of $K(T)$ using the same type of arrangement as in Ref. 1, but we used an 2-mm EPR spectrometer.

The experiments were performed in a 5.1-T field. In such a magnetic field, H atoms have a considerable degree of electronic-spin polarization (of the order of 0.99 at $T \simeq 1.35$ K), so that it was first necessary to determine the magnetic field dependence of K. However, the recombination rate of H atoms in solid H_2 does not depend on the field for fields at least up to 5.1 T and temperature above 1.35 K. This allows us to ignore the influence of the magnetic field on the diffusion and recombination when analyzing the results.

The experimental arrangement was analogous to that in Ref. 1 and, briefly, reduced to the following. The mixture of hydrogen atoms and molecules, formed in an rf discharge, condensed on a cold substrate (sapphire at $T \sim 1.5$ K), located inside the working resonator of the EPR spectrometer. After the sample was created, the amplitudes of the EPR signal, $A(t)$, of H atoms in the specimen were measured as a function of time. The initial concentration of atoms in the specimens was approximately the

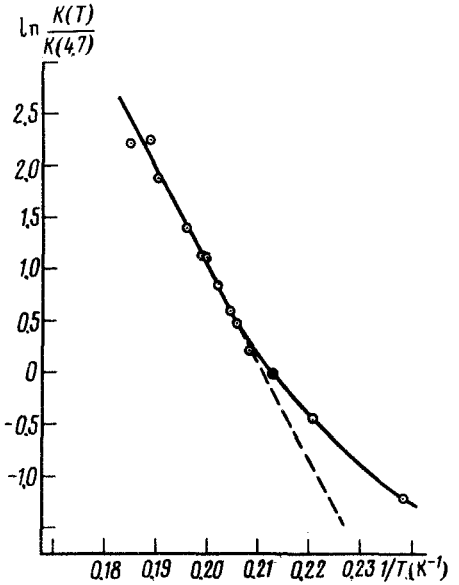

FIG. 1. $K(T)$ for H atoms in solid H_2 for 4.2 K$\leqslant T \leqslant$5.4 K.

same as in Ref. 1 ($10^{-4} < N_i/N_{H_2} < 10^{-3}$) and a factor of 3–4 greater than in Refs. 2 and 3, due to the improved construction of the dissociator and atom conduit. At all temperatures the quantity $1/A$ depended linearly on t, indicating a second-order recombination law. For each specimen, the measurements were performed at several temperatures and the ratio $K(T)/K(T_0)$ was measured. ($T_0 = 4.2$ K for the region $1.35 \leqslant T \leqslant 4.2$ and $T_0 = 4.7$ K for $4.2 \leqslant T \leqslant 5.4$ K.)

The temperature dependence $K(T)$ ($T \geqslant 4.2$ K) in coordinates $\ln K(T)/K(T_0)$ $1/T$ is shown in Fig. 1. The reaction rate for $T \gtrsim 4.75$ K is determined almost entirely by the classical diffusion process, since the experimental dependence is well described by the expression $K(T) = K_0 \exp(-E_a/T)$, where the activation energy $E_a = 103 \pm 5$ K, consistent with the results in Ref. 1.

The temperature dependence $K(T)$ for the region 1.35 K$\leqslant T \leqslant$4.2 K is shown in Fig. 2. In Fig. 2(a) the results are presented in the coordinates $\ln[K(T)/K(4.2)]$, $\ln(T/1$ K) in order to determine the law governing the temperature dependence; from here we find that $K(T) \sim T^{0.98 \pm 0.05}$. In Fig. 2 the same experimental points are shown using a linear scale. At $T = 4.2$ K the value of the constant that is obtained when the contribution corresponding to the classical process is subtracted from the experimental value is also presented. This value falls on the continuation of the linear law, occurring for $T < 4$ K in the region $T \cong 4.2$ K, which confirms the additivity of the above-barrier (classical) and subbarrier (quantum) diffusion processes.

Discussion of results. In the temperature range $T \gtrsim 4.75$ K, the recombination reaction rate is determined by classical diffusion with $E_a = 103 \pm 5$ K. For 1.35 K$\leqslant T \leqslant$4 K, the law $K(T) \sim T^{0.98 \pm 0.05}$ indicates the fact that the recombination processes are determined by quantum diffusion of atomic hydrogen and, in addition, the

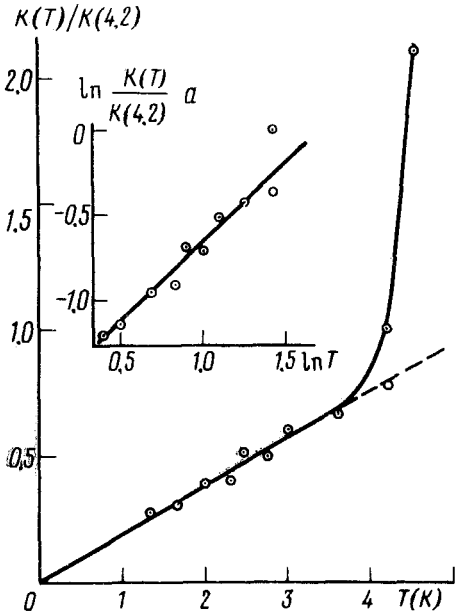

FIG. 2. $K(T)$ for H atoms in solid H_2 for 1.35 K$\leqslant T \leqslant$4.2 K.

temperature dependence of the diffusion coefficient is very nearly linear. This result agrees with the results of the theory of quantum diffusion in irregular systems, developed by Yu. Kagan *et al.* (see Refs. 4 and 5). As shown in these references, the displacement of the energy levels of particles in equivalent wells in the crystal matrix leads to localization of the diffusing particles. Their diffusion becomes possible only due to interaction with phonons. In addition, an increase in temperature leads to delocalization of particles, and the diffusion coefficient increases. For recombination, hydrogen atoms must approach to atomic distances, which forces a particle to pass through the zone of large displacement. As a result, in the region of large displacement single-phonon processes begin to play a decisive role, which leads to the linear temperature dependence of the diffusion coefficient.[4,5] It has not been ruled out that the large displacement of levels could be attributed to a large number of defects in the specimens.

The results obtained agree with the ideas on quantum diffusion in irregular systems developed by Yu. Kagan *et al.* The linear temperature dependence of the diffusion coefficient proves the existence of a new type of quantum diffusion when there is a large displacement of levels.

Remarks on the magnetic-field independence of the recombination rate. We can easily estimate from our experimental data (the concentration half-life in the specimens is of the order 10^4 s at concentrations of the order of 10^{-4}–10^{-3}) the lifetime of an atom in a single position in the matrix. This lifetime is of the order of 1–10 s. As shown in Refs. 2 and 3, the relaxation time of an electron spin of a hydrogen atom at $T \cong 1.3$ K in a field $B \cong 5$ T, is $\tau_p \sim 10^{-2}$ s, while the spin depolarization time, for this

reason is $\tau_f = \tau_p \exp(2\mu B/T) \sim 1$ s. Thus, when the atom is located in some position in the matrix, its spin can change orientation and if another hydrogen atom is located next to it, then they recombine, i.e., the influence of the magnetic field on the reaction rate is eliminated. The exponential dependence of τ_f on the ratio B/T suggests that by doubling this factor it will be possible to observe the influence of the magnetic field on the reaction rate.

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