

# Anomalous temperature dependence of the ESR line width of hydrogen atoms in crystalline molecular hydrogen

A. S. Iskovskikh, A. Ya. Katunin, I. I. Lukashevich, V. V. Sklyarevskii,  
and V. A. Shevtsov

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First experimental results are reported on the time evolution of the width of the ESR line of H atoms in solid H<sub>2</sub> for various ortho-para compositions in the temperature interval  $1.6 < T < 5.7$  K. The line width and its temperature dependence are governed primarily by the interaction of H atoms with the ortho-subsystem of the H<sub>2</sub> crystal.

The previous use of the ESR method to study the behavior of H and D atoms in solid hydrogen led to the discovery of the quantum diffusion of impurity atoms<sup>1,2</sup> and the quantum isotope-exchange reaction.<sup>3</sup> These studies focused primarily on that information on the total number of atoms in the sample which was incorporated in the integral intensity of the ESR spectrum. Improvements in the experimental procedure have made it possible to reduce the instrumental broadening of the ESR line to  $\sim 0.1$  Oe. This progress has opened the door to the extensive information on the interaction of impurity atoms with the lattice which is incorporated in the width of the ESR line.

The samples in the present experiments are synthesized by condensing an atom-molecule mixture from an rf discharge on a cold substrate.<sup>1,2</sup> In addition, during the synthesis of the samples we have the option<sup>3</sup> of condensing a flow of para-H<sub>2</sub> or normal H<sub>2</sub> at the same time as the atom-molecule mixture from the rf discharge, so that the ortho-para composition of the matrix can be varied.

In the present experiments, in contrast with Refs. 1–3, it turned out to be possible to measure the absolute number of molecules in a sample. This capability made it possible to determine the absolute concentrations of the atoms, which reached maximum values of 0.02–0.04% for our samples of “H in H<sub>2</sub>.”

**Experimental results.** The spectrometer used in the present experiments measures the derivative of the ESR absorption signal,  $d\chi''(H)/dH$ , as a function of the strength of the polarizing magnetic field  $H$  (see the inset in Fig. 1). Consequently, we selected the distance between the maxima of the derivative,  $\Delta$ , as a measure of the line width. We should point out that the results reported here were obtained in the absence of saturation of the corresponding ESR transitions. Furthermore, there was no modulation line broadening, and the results do not depend on the frequency of the magnetic-field modulation in the range from 400 Hz to 30 kHz. In all of the experiments, the line shape remained symmetric, and the resonant field remained constant within  $\pm 0.1$  Oe.

1. Figure 1 shows the synchronous changes at various temperatures in the absolute concentration of H atoms in the H<sub>2</sub> matrix (schematically) with an ortho-H<sub>2</sub> concentration  $C_{o-H_2} = 0.75$  and in the width ( $\Delta$ ) of the first line in the spectrum of H atoms (the width of the second line behaves in a similar way. The initial line width,  $\Delta(0)$ , did not exceed 1.2 Oe in any of the samples. The origin for the time scale in this figure is the time at which synthesis of the sample ends. It can be seen from Fig. 1 that the primary narrowing of the line occurs against the background of a significant recombination of atoms. Varying the temperature over the interval 1.6–4.4 K does not affect the monotonic course of the primary contraction. After a sufficiently long expo-

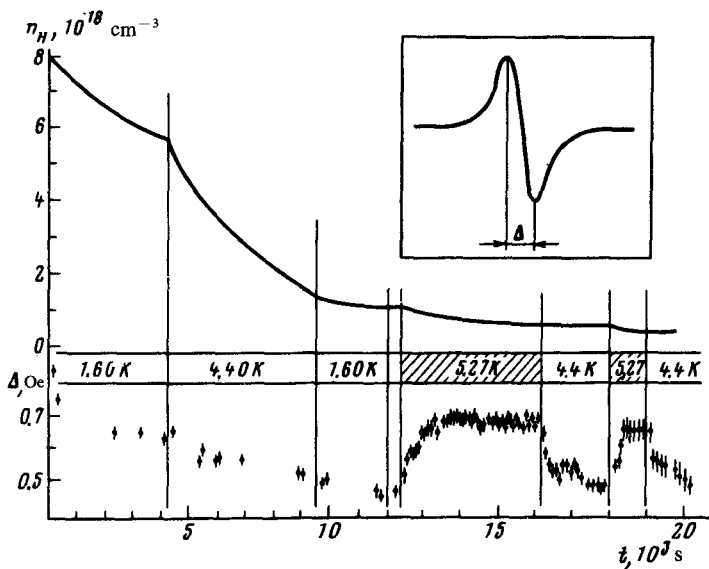


FIG. 1. Time evolution of the absolute concentration of H atoms in H<sub>2</sub> (top) and of the width of the ESR line (bottom) at various temperatures.

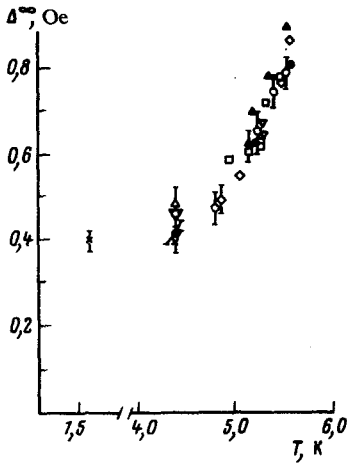


FIG. 2. Temperature dependence of the line width,  $\Delta^\infty(T)$  ( $C_{o-H_2} = 0.75$ ).

sure, the line width reaches 0.40–0.45 Oe in the course of the primary contraction.

2. A further temperature change in the interval 1.6–4.4 K does not change the width of the (already contracted) line. At the same time, raising the temperature above 4.5 K causes the width  $\Delta(t, T)$  to begin to increase (Fig. 1) with a scale time of 10–100 s; then it reaches the value  $\Delta^\infty(T)$ . The time required for the sample temperature to stabilize is no more than a few seconds (this time can be estimated by using the Curie law for the integral intensity of the ESR signal). The concentration of atoms continues to decrease during the secondary broadening of the line. Figure 2 shows the behavior

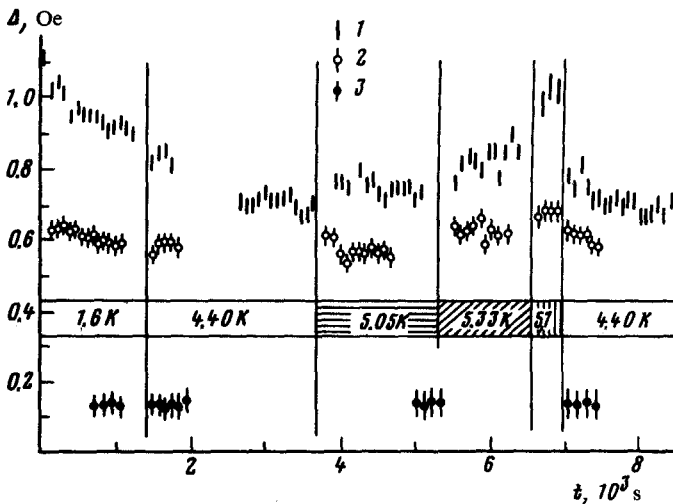


FIG. 3. Time evolution of the width of the ESR line of H in  $H_2$  at various temperatures and for various concentrations of ortho- $H_2$ : 1— $C_{o-H_2} = 0.75$ ; 2— $C_{o-H_2} = 0.20 \pm 0.02$ ; 3— $C_{o-H_2} < 0.01$ .

$\Delta^\infty(T)$  found for several samples. The secondary broadening of the line is thus determined by the temperature and does not depend on the concentration of atoms.

3. A further lowering of the temperature to  $T \lesssim 4.5$  K results in a secondary contraction of the line (Fig. 1). The value of  $\Delta$  tends toward the value reached in the primary contraction. We see from Fig. 1 that the concentration of atoms remains essentially constant in the course of the secondary contraction (in contrast with the behavior during the primary contraction).

4. Figure 3 shows the results of some similar experiments with three "H in H<sub>2</sub>" samples with various ortho-para compositions and approximately identical initial concentrations of atoms. We see from this figure that a reduction of the concentration of ortho-H<sub>2</sub> causes the initial line width to decrease significantly, while the primary contraction, the secondary contraction, and the secondary broadening all become less pronounced. The interaction of atoms with the ortho-subsystem of the H<sub>2</sub> crystal thus contributes substantially to the width of the ESR line of the H atoms and to its temperature dependence. Furthermore, a lowering of  $C_{o-H_2}$  increases the spin-lattice relaxation time of the H atoms. In a sample with  $C_{o-H_2}$  this time is on the order of a few seconds.

**Discussion of results.** The width of the ESR line of H atoms in an H<sub>2</sub> crystal is determined primarily by the dipole interaction of the electron spin magnetic moments of the atoms with each other and with the nuclear magnetic moments of the surrounding orthomolecules. The strong dependence of the line width on the ortho-para composition of the matrix indicates that the latter interaction is dominant. For the immobile H atoms at sites of the hcp H<sub>2</sub> lattice, the dipole interaction with the ortho-H<sub>2</sub> should lead to a line with a Gaussian shape<sup>4,5</sup> and a width  $\Delta = 2\sqrt{\langle H^2 \rangle} \approx 4.0\sqrt{C_{o-H_2}}$  Oe. For normal hydrogen ( $C_{o-H_2} = 0.75$ ) we have  $\Delta \approx 3.5$  Oe, which is nearly three times the maximum line width observed experimentally. We believe that there are two factors which could cause such a significant discrepancy. First, since the energy of the zero-point vibrations of the H atoms and of the H<sub>2</sub> molecule in the lattice is far greater than the energy of the H-o-H<sub>2</sub> dipole interaction, the dipole interaction must be averaged over the vibrational ground state in the Van Vleck theory.<sup>4,5</sup> Because of the significant delocalization of the H atom, this averaging can in principle lead to a significant decrease in the dipole contribution to the line width. Second, the H atom may "stimulate" a comparatively rapid conversion of the closest orthomolecules into parap-H<sub>2</sub> ( $I = 0$ ); this mechanism would again effectively lower the dipole contribution to the line width.

An explanation for the anomalous temperature dependence  $\Delta(t, T)$  should also be sought in the corresponding temperature-induced changes in the H-o-H<sub>2</sub> interaction. This interaction may be changed by, for example, the following factors: a) a decrease in the local o-H<sub>2</sub> concentration near an H atom because of a competition between the stimulated ortho-para conversion and diffusion; b) the transitions of atoms between different types of positions in the lattice, differing in the number of nearest o-H<sub>2</sub> molecules and/or the distance from them (sites, interstitial positions, etc.) and also the degree to which this interaction is averaged over the zero-point vibrations of the atom in the different positions. It can be shown that in the case of a homogeneous diffusion coefficient for the atoms in the crystal, an explanation of the observed effects in terms

of factor a) would require that the scale time for the conversion of the nearest o-H<sub>2</sub> molecule be short in comparison with the diffusion time of an atom in the crystal (10–0.1 s at 1.3 < T < 5.5 K).<sup>1,2</sup> In the “H in H<sub>2</sub>” samples with atomic concentrations ~ 10<sup>-4</sup>, the total number of o-H<sub>2</sub> molecules must decrease substantially during the experiment, in contradiction of the observed dependence of the secondary broadening and the secondary contraction on the ortho-para composition. In the case of nonuniform quantum diffusion in an irregular crystal,<sup>6</sup> however, we could not rule out the possibility that factor a) might be required to explain such effects. A more likely explanation, in our opinion, is possibility b), that there exist several types of sites for H atoms in the lattice. It must be assumed that large ground-state energies correspond to positions with a stronger H-o-H<sub>2</sub> interaction. A situation of this sort naturally arises if the difference in the interaction with the ortho-H<sub>2</sub> is due to a difference in the degree to which the dipole interaction is averaged over the zero-point vibrations of the atom: In positions in which the atoms are more localized, the energy of the zero-point vibrations will be higher. According to this model, the temperature dependence  $\Delta^\infty(T)$  is determined by the temperature dependence of the populations of the different types of positions. The dynamic nature of the dependence  $\Delta(t, T)$  is caused by the scale time for the relaxation to equilibrium populations in the course of the diffusion of atoms through the crystal. This diffusion must occur primarily along positions with the lowest energy, which are separated by the lowest barriers (~ 105 K).<sup>2,1</sup> At the same time, different types of positions may be separated by higher barriers, so that the scale times for relaxation to the equilibrium populations of the different types of positions (even if they are side-by-side: a site beside an interstitial position) may be significantly longer than the lifetimes in a single trapping center which are found from data on recombination.<sup>1,2</sup> The line widths in each of the types of positions and thus the difference between them are determined by the value of  $C_{o-H_2}$ , as is found experimentally.

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