H and N atoms in a para-H_2 crystal. 2. Investigation of electron spin relaxation processes

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The electron spin-lattice relaxation processes of atomic hydrogen and nitrogen in para-H_2 crystals are investigated. It is demonstrated that the relaxation of H and N atoms at the orthomolecules in all probability follows the same phonon-free mechanism. Phonon-mediated relaxation at the N_2 molecules is very effective for atomic nitrogen.

INTRODUCTION

It has been demonstrated[1] for atomic hydrogen in para-H_2 from an analysis of pumping of the forbidden electron-nuclear transitions that the atomic hydrogen diffusion rate near the orthomolecules is $\leqslant 10^{-17}$ cm^2/s at $T = 1.5$–4.2 K.[1] Information on this diffusion rate can also be recovered by analyzing electron spin-lattice relaxation of atomic hydrogen in parahydrogen. This problem was the subject of Ref. 2, which demonstrated that the relaxation rate is determined by the interaction of H atoms with ortho-H_2 and follows a phonon-free mechanism. One possible phonon-free atomic hydrogen relaxation mechanism was proposed in Ref. 3. This mechanism requires quantum diffusion of the atom near the ortho-H_2 for relaxation. The bandwidth for quantum diffusion of the H atoms was estimated at $\Delta \sim 10^{-1}$ K.

To determine the role of the distribution functions of the hydrogen atom near the ortho-H_2 in the spin-lattice relaxation process we examine the relaxation of N atoms in parahydrogen in this paper. Since the mass of the N atom is far greater than that of the hydrogen atom, such an atom diffuses extraordinarily slowly at temperatures of 1.5–4.2 K.[1)] This means that the pattern of atomic nitrogen relaxation at orthomolecules differs significantly from that observed for atomic hydrogen if the relaxation process for atomic hydrogen is related to quantum diffusion.

1. EXPERIMENTAL METHOD

1.1. Fabrication of the samples

The method of producing samples of "H in para-H_2" and "N in para-H_2" has been described in detail in Ref. 1. At this juncture it is worth noting that the orthomolecule concentration in the parahydrogen crystals in this paper was determined from the pumping rate of the forbidden electron-nuclear transformations for atomic hydrogen and nitrogen.[1] A separate third channel was used to obtain the N_2 dopant in the samples of "N in para-H_2" by direct application of the nitrogen molecules to a cold substrate in conjunction with an atomic N beam and a para-H_2 molecular beam. The N_2 molecular concentration was defined as the ratio of the paramolecule and nitrogen molecule streams on the substrate. This relation was determined experimentally by injecting normal hydrogen on a third channel and comparing the orthomolecular concentration in the resulting sample to experimental results in which para-H_2 was mixed with normal hydrogen in the feed system.[1]

The resulting samples had the following composition: "H in para-H_2," concentration of $C_{\rm H}$ atoms $\sim 10^{-5}$, concentration of $C_{\rm O}$ orthomolecules $\sim 2.5 \cdot 10^{-3}$–$3 \cdot 10^{-2}$; "N in para-H_2:" concentration of $C_{\rm N}$ atoms $\sim 10^{-6}$, concentration of $C_{\rm O}$ orthomolecules $\sim 2 \cdot 10^{-3}$–$3 \cdot 10^{-2}$, concentration of N_2–C_{N_2} molecules, $\sim 5 \cdot 10^{-4}$–$2 \cdot 10^{-2}$.

Note that certain measures were taken to minimize the quantity of molecular oxygen in our samples. The O_2 molecular dopant level was therefore less than 10^{-6} and had no effect on the relaxation rate of the hydrogen or nitrogen atoms.

1.2. Measurement of the relaxation rate

The features of the EPR spectra of atomic hydrogen and nitrogen as well as their recording conditions are examined in detail in Ref. 1. The well-known method in EPR technology of restoring magnetization after line saturation[2] was used to determine the spin-lattice relaxation time in this study. One of the hyperfine structure (HFS) lines occurred was totally saturated over a time of ≈ 0.3 s at a microwave power of $\sim 10^{-3}$ W by linear tuning of a magnetic field through resonance.[5] This line was therefore recorded in a time interval t. Figure 1 shows the dependence of the amplitude of a single HFS line of atomic nitrogen on the time period following total saturation of this line. Clearly in this case the relation is described with satisfactory accuracy by the exponent

$$A = A_0(1 - \exp(-t/T_1)) \tag{1}$$

with a characteristic time $T_1 = 9.6 \pm 0.3$ s which in this case also represents the spin-lattice relaxation time.

Note that the instrumentation used in our experiments made it possible in most cases to control the field intensity of the principal magnetic field from 1700 through 5200 Oe within a time much less than T_1. This made it possible to hold the sample in different magnetic fields and thereby obtain the dependence of the relaxation rate on the splitting level between the Zeeman sublevels of atomic hydrogen and nitrogen in the time t between saturation and the recording of the HFS transition.

2. RESULTS FROM EXPERIMENTS ON THE RELAXATION RATE OF H AND N ATOMS IN PARA-H_2

It should be noted at the outset that the relaxation rate of H and N atoms in para-H_2 depends on a multitude of

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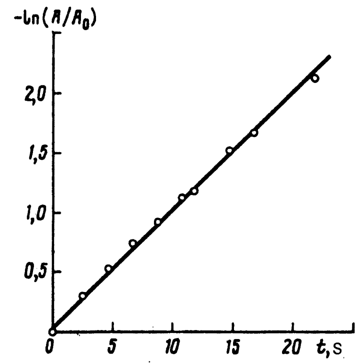

FIG. 1. Amplitude of a single HFS line of atomic N plotted versus the post-saturation time of this line. On the ordinate axes one should read: $[-\ln(1-A/A_0)]$.

parameters: the ortho-H_2 concentration (as well as the molecular N_2 concentration for atomic N), temperature, the intensity of the magnetic field in which the saturation occurred, and the post formation time of the sample. This substantially complicates the process of comparing the relaxation of atomic hydrogen and nitrogen on orthomolecules. It was nonetheless possible to determine the contribution to the total relaxation rate of atomic N relaxation on ortho-H_2 as well as the contribution of relaxation on N_2 molecules by manipulating the composition of the "N in para-H_2" samples. This made it possible to compare the results to the data from Ref. 2 for atomic hydrogen relaxation on orthomolecules. The dependence of the relaxation rate on the post-formation time and the dependence of T_1^{-1} on the concentration of ortho-H_2 were also refined for atomic hydrogen.

2.1. Dependence of T_1^{-1} on the post formation time of the sample

It turned out from our analysis of the relaxation processes of atomic hydrogen and nitrogen in parahydrogen that the relaxation rate decreases with time following fabrication of the sample to a varying degree depending on the composition of this sample. The value of T_1^{-1} remains constant within measurement error for atomic nitrogen only if the relaxation rate is determined by the concentration of N_2 molecules in the sample (see Fig. 2a). If the relaxation rate is determined by the concentration of ortho-H_2, there is a reduction in the relaxation rate with a characteristic time ~ 1 h (Fig. 2) following fabrication of the sample for both the H and the N atoms.

At ortho-H_2 concentrations of $\sim (2\text{–}4)\cdot 10^{-3}$ the ratio of the steady state relaxation rate to the rate measured immediately following fabrication of the sample is $\sim 0.3\text{–}0.5$ for the N atoms and 0.03–0.1 for the H atoms. At high orthomolecule concentrations this ratio grows to 0.6–0.8 for both the atomic nitrogen and the atomic hydrogen. Note that both the characteristic decay time of the relaxation rate and the ratio of the steady state relaxation rate to the initial rate are virtually independent of the temperature at which the sample is held (see Fig. 2b for the sample of "H in para-H_2).”

The value of T_1 obtained over a 3–5 h period will subsequently remain virtually unchanged. The characteristic time of a further decay in the relaxation rate is greater than 100–200 h for the sample of "H in para-H_2" with $C_O = 1.5\cdot 10^{-2}$ (see Fig. 2b) for $t > 10^4$ s.

Unless stipulated otherwise, the steady state relaxation rate will henceforth be used for T_1.

2.2. Dependence of T_1^{-1} on sample temperature and concentration of ortho-H_2 (for atomic H and N) and N_2 molecules (for atomic N)

a. Atomic nitrogen

Figure 3a shows the temperature dependence of the relaxation rate of N atoms in para-H_2 for different orthomolecule concentrations of the sample, but with a fixed N_2 concentration. Figure 3b provides analogous relations for samples with the same concentration of orthomolecules and different molecular nitrogen concentrations. By comparing these relations we find that there are two independent relaxation channels for the nitrogen atoms: relaxation on ortho-H_2 and relaxation on the N_2 molecules. In the first case, the relaxation rate is rather weakly temperature-dependent (see, for example, Figure 3a for $C_O = 3.2\cdot 10^{-2}$), while in the second case the temperature dependence is significantly stronger (Fig. 3b). The dependence of the relaxation rate of atomic N on the concentration of orthomolecules and N_2 molecules at a temperature 1.6 K is shown separately in Figs. 4 and 5.

The two independent relaxation channels for the N atoms confirms that all experimental results (80 points) are satisfactorily described by a function

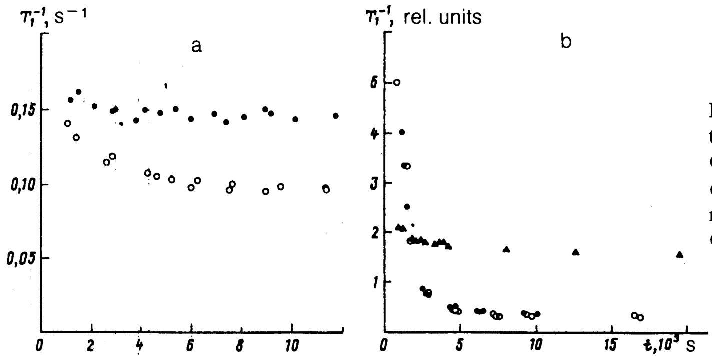

FIG. 2. The relaxation rate of H and N atoms in para-H_2 plotted versus time ($t < 9\cdot 10^2$ s: fabrication of the sample), a—"N in para-H_2": ○—$C_O = 2.7\cdot 10^{-2}$, $C_{N_2} = 10^{-3}$, $T = 1.6$ K; ●—$C_{N_2} = 2\cdot 10^{-2}$, $C_O = 2\cdot 10^{-3}$, $T = 1.6$ K; b—"H in para-H_2": ●, ○—$C_O = 2.5\cdot 10^{-3}$, 1 rel. units $= 10^{-2}$ s^{-1}, $T = 1.6$ K (●), $T = 4.2$ K (○); ▲—$C_O = 1.5\cdot 10^{-2}$, $T = 1.6$ K, 1 rel. units $= 10^{-1}$ s^{-1}.

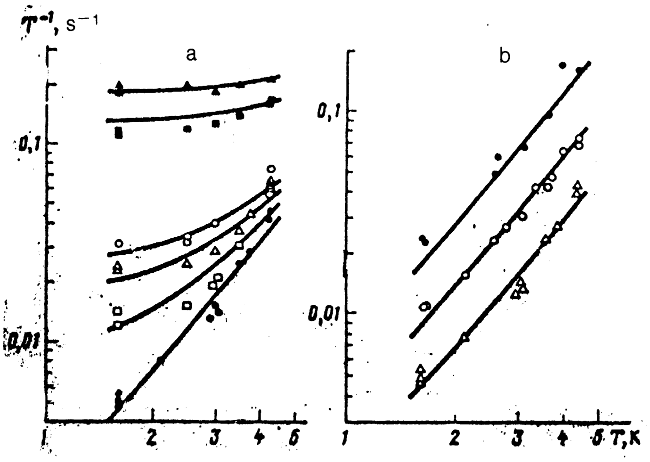

FIG. 3. Relaxation rate of atomic N in para-H_2 plotted as a function of the temperature of the sample: a—$C_O = 2\cdot 10^{-3}$(●); $7\cdot 10^{-3}$(□); 10^{-2}(△); $1.2\cdot 10^{-2}$(○); $2.7\cdot 10^{-2}$(■); $3.2\cdot 10^{-2}$(▲); $C_{N_2} = 5\cdot 10^{-4}$ in all samples; b—$C_{N_2} = 5\cdot 10^{-4}$(△); $1.2\cdot 10^{-3}$(○); $2\cdot 10^{-3}$(●); $C_O = 2.5\cdot 10^{-3}$ in all samples.

$$T_1^{-1}=k_1C_o^{\alpha}+k_2C_{N_2}^{\beta}T^{\gamma}. \qquad (2)$$

The first term corresponds to relaxation on orthomolecules, while the second corresponds to relaxation on N_2 molecules. The parameter values in Eq. (2) and their errors are given below:

k_1	k_2	α	β	γ
$(2,2\pm0,4)\cdot10^2$	$1,8\pm0,5$	$2,1\mp0,3$	$0,9\pm0,1$	$2,3\mp0,3$

while Figs. 3–5 present the corresponding cross sections of function (2).

We can therefore state that the relaxation rate of N atoms on orthomolecules is indeed weakly dependent on temperature and grows as a function of concentration of the orthomolecules as $T_1^{-1} = (2.2 \pm 0.4)\cdot 10^2 C_O^{2.1\pm0.3}$ s^{-1}.

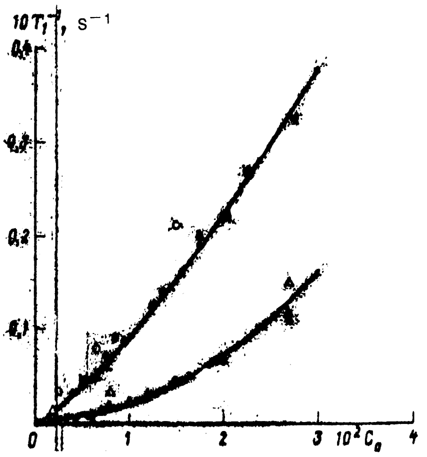

FIG. 4. Relaxation rate of atomic H and N in para-H_2 versus the concentration of orthomolecules in the sample: ▲, △—"N in para-H_2", $C_{N_2} = 5\cdot 10^{-4}$, $T = 1.6$ K; ●, ○—"H in para-H_2", $T = 1.6$ K; ▲, ●—the steady state relaxation rate; △, ○—the relaxation rate measured 10^3s after the beginning of fabrication of the sample.

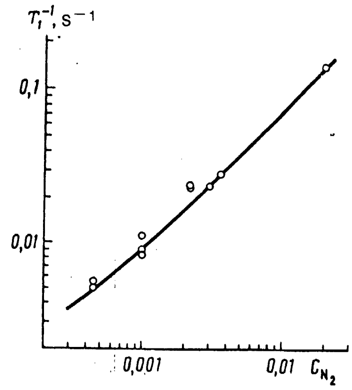

FIG. 5. The relaxation rate of N atoms in para-H_2 versus the N_2 molecular concentration ($C_O = 2\cdot 10^{-3}$, $T = 1.6$ K).

b. Atomic hydrogen

As is the case with the relaxation rate of N atoms on ortho-H_2, the relaxation rate of hydrogen atoms on the orthomolecules is weakly dependent on temperature.[2] The corresponding data for the relation $T_1^{-1}(C_O)$ are listed in Fig. 4. These data are satisfactorily described by the power function:[2)] $T_1^{-1} = (9.1 \pm 0.1)\ C_O^{1.3\pm0.1}$ s^{-1}.

The H atoms have poor relaxation on the N_2 molecules. Doping the para-H_2 with $5\cdot 10^{-3}$ hydrogen alters the relaxation rate of the atomic hydrogen in the crystal by less than 10^{-2} s^{-1} at $T = 1.6$–4.2 K.

2.3. The dependence of T_1^{-1} on the magnitude of the magnetic field in which relaxation occurs

The dependence of the relaxation rate of atomic nitrogen on the splitting level between the Zeeman sublevels E_z was measured on two samples of "N in para-H_2." We had $C_O = 7\cdot 10^{-3}$, $C_{N_2} = 5\cdot 10^{-4}$ for the first sample and $C_O = 2\cdot 10^{-3}$, $C_{N_2} = 5\cdot 10^{-4}$ for the second sample.

The relaxation rate is primarily determined by relaxation on the orthomolecules for the first sample for $T = 1.6$ K. The ratio of the relaxation rates at ortho-H_2 and the N_2 molecules at this temperature is approximately 5 [see Eq. (2)]. In this case, as we see from Fig. 6a, the relaxation rate decreases with increasing magnetic field. The same result

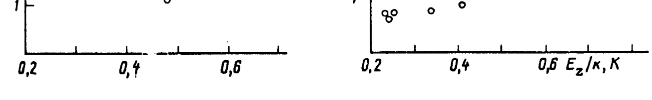

FIG. 6. The relaxation rate of N atoms in para-H_2 versus the splitting level between the Zeeman sublevels: a—$C_O = 7\cdot 10^{-3}$, $C_{N_2} = 5\cdot 10^{-4}$, $T = 1.6$ K; b—$C_O = 2\cdot 10^{-3}$, $C_{N_2} = 5\cdot 10^{-4}$, $T = 1.6$ K (○), $T = 3$ K (●).

was obtained for H atoms in para-H_2 (Ref. 2).

Relaxation at N_2 molecules makes the primary contribution to T_1^{-1} for the second sample. Figure 6b shows the results of measuring $T_1^{-1}(E_z)$. It is clear that unlike relaxation at orthomolecules, the relaxation rate at the N_2 molecules grows with increasing magnetic field.

2.4. Dependence of T_1^{-1} on the atomic concentration in the sample

According to reported data[2] the relaxation rate of atomic hydrogen is independent of the concentration of the atoms and is easily detected in the recombination process. Unlike hydrogen atoms, N atoms recombine at para-H_2 at a significantly slower rate compared to crystal sublimation. Nonetheless it was possible to fabricate samples with an atomic nitrogen concentration of $\sim 10^{-5}$ by altering the accommodator temperature. The relaxation times of atomic N in the samples at all temperatures in the range 1.6–4.2 K were at least a factor of 2 lower than the corresponding values of T_1 for the samples of "N in para-H_2" with an atomic nitrogen concentration of $\sim 10^{-6}$. The observed difference is likely to be due to the additional molecular N_2 dopant in samples with the higher atomic nitrogen concentration. In any case this difference is much less than the difference in the atomic concentration and we can state that the relaxation rate of the N atoms on one another will make no significant contribution to the relaxation rates observed in our experiments.

3. DISCUSSION OF EXPERIMENTAL RESULTS

3.1. Relaxation of atomic H and N in ortho-H_2

As demonstrated above, the relaxation rate of atomic H and N in ortho-H_2 depends weakly on the sample temperature and decreases with increasing magnetic field. Moreover, the absolute relaxation rates were similar at an identical orthomolecular concentration. The observed differential of a factor of 2–3 can be attributed to the stimulated conversion of orthamolecules near the dopant atoms.(3)

It follows that the spin-lattice relaxation of hydrogen and nitrogen atoms at dopant orthomolecules in para-H_2 follows the same phonon-free mechanism. If so, this mechanism is independent of atomic diffusion, since the nitrogen atoms are treated as immobile.

The following phonon-free relaxation mechanism can be proposed as a possible explanation for these experimental results. We know that ortho-H_2 molecules have a rotational magnetic moment $\mu_r = 0.88_N$ where μ_N is the Bohr magneton. The electrical quadrupole-quadrupole interaction of the orthomolecules causes reorientation of their rotational moments and, consequently, will modify the directions μ_r. If a dopant atom is located near the orthomolecule, this produces a resulting oscillating magnetic field and longitudinal relaxation of the electron spin of this atom becomes possible. The Zeeman energy of the atom is converted in this case into quadrupole-quadrupole interaction energy of the orthomolecules and is then contributed to the lattice. The rate of such a process depends on the atom-orthomolecule distance as $1/R^6$ and hence relaxation will only be effective for atoms near the ortho-H_2. All remaining atoms in the sample can relax by spin diffusion to the atoms near the orthomolecules.(4)

Such a relaxation mechanism where the Zeeman energy is contributed to the quadrupole subsystem has been considered in an analysis of the nuclear relaxation of ortho-H_2 in parahydrogen.[8] This study demonstrated that if the Zeeman energy exceeds the quadrupole-quadrupole interaction level of orthomolecules at an average distance (this condition always holds in our samples for electron spin relaxation), the relaxation rate is independent of temperature, decreases with increasing magnetic field as $1/H^{7/4}$ and is dependent on the orthomolecular concentration as $C_O^{5/4}$. Using the results from Ref. 8 we show that the relaxation rate following this mechanism is independent of temperature for electron spin and decreases with magnetic field as $1/H^{7/4}$. The dependence of the relaxation rate on the concentration of orthamolecules is stronger: $T_1^{-1} \propto C_O^{9/4}$. This is because only a small fraction of the atoms are near the ortho-H_2.

The proposed relaxation mechanism of the dopant atoms is therefore suitable for a qualitative description of the majority of these experimental results. There are, however, a number of difficulties in explaining the results of the experiment in terms of this mechanism.

1. A somewhat weaker dependence of the relaxation rate on orthomolecule concentration compared to the theoretical value is observed for atomic hydrogen, $\propto C_O^{1.3}$.

2. We did not succeed in explaining the dependence of the relaxation rate of atomic N or H on the post-formation time of the sample.(5)

3.2. Relaxation of N atoms on N_2 molecules

The increase in the relaxation rate with increasing temperature and magnetic field suggests that in this case spin-lattice relaxation is phonon-mediated. The relaxation rate is nearly two orders of magnitude faster at 4.2 K than the relaxation of atomic nitrogen on orthomolecules and is 3–4 orders of magnitude faster than would be expected for ordinary dipole relaxation of N atoms at N_2. This may be both because the interaction of N atoms with nitrogen molecules is stronger than that due to the dipole-dipole interaction, and because the vibrational spectrum of a heavy N_2 molecule in the lattice may differ significantly from the phonon spectrum of a para-H_2 crystal.

CONCLUSION

This paper has demonstrated that the electron spin-lattice relaxation of N atoms in para-H_2 follows two independent channels. One is relaxation on the ortho-H_2 and the other is relaxation on the N_2 molecules.

In the first case the relaxation process follows a zero-phonon mechanism and this mechanism appears to be identical for both atomic hydrogen and nitrogen. If this is the case, the diffusion of these atoms has little effect on the zero-phonon relaxation rate, since the nitrogen atom can be treated as fixed.

This paper also proposes a zero-phonon spin-lattice relaxation mechanism that is different from the mechanism examined in Ref. 3. This mechanism, which is related to the conversion of the Zeeman energy of the atom into quadrupole-quadrupole interaction energy of the orthomolecules, provides a qualitative explanation for the majority of experimental results reported in this paper and in Ref. 2.

Unlike relaxation at the ortho-H_2, the relaxation of N atoms at N_2 molecules is a phonon-mediated process. The specific mechanism of this relaxation process requires a more comprehensive theoretical analysis.

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[1] Strictly speaking this refers to the diffusion rate of the atom relative to the orthomolecules in the crystal. However, this is only significant for $T > 4.2$ K. By extrapolating the data reported in Ref. 4 we easily find that the vacancy diffusion rate of ortho-H_2 is much less than 10^{-17} cm^2/s for $T < 4.2$ K. Consequently, the N atoms, at least in this temperature range, can be treated as immobile compared to the hydrogen atoms.

[2] The relations $T_1^{-1}(C_O)$ provided here apply only to the steady state relaxation rate. Figure 4 provides for comparison purposes the initial relaxation rate for several samples of "H in para-H_2" and "N in para-H_2."

[3] As we know, the conversion rate for dopant atom-stimulated conversion is proportional to the square of the magnetic moment of the atom in hydrogen.[6] This means that the local concentration of orthomolecules near the hydrogen atom is lower than near an H atom due to conversion. Obviously, the relaxation rate for the N atoms with all other conditions remaining equal will be less than for the hydrogen atoms. The data listed in Fig. 4 provide a qualitative confirmation of this conclusion.

[4] We must emphasize that spin diffusion is not the limiting stage in the relaxation process for either the H or the N atoms. According to Ref. 7 this follows from the exponential nature of the relaxation curves for atomic hydrogen and nitrogen as well as the reported data[1] on the spin diffusion rate of atomic H and N in para-H_2.

[5] The reduction in the relaxation rate of H and N atoms on ortho-H_2 depending on the post-fabrication time of the sample is directly related to the relaxation mechanism of these atoms. Data[1] from pumping of the forbidden electron-nuclear transitions for atomic H and N suggest that the characteristic time to a local distribution of the ortho-H_2 concentration near the atom is $\leqslant 10^3$ s. This means that the reduction in T_1^{-1} following the fabrication of the sample ($t > 10^3$ s) cannot be attributed to conversion of the orthomolecules near the dopant atom.

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