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# ON THE PARAMAGNETISM OF DPPH

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Summary. - The static magnetic susceptibilities of the organic free radical  $\alpha, \alpha'$ -diphenyl- $\beta$ -picryl-hydrazyl (DPPH) have been measured using the Faraday method. The paramagnetism of the sample, in which the radicals are separated by deuterated benzene, fits the Brillouin function for non-interacting paramagnetic centres each having a magnetic moment due to the spin of a single unpaired electron. At temperatures below 4 K, however, a systematic deviation is observed. The paramagnetism of a solvent-free DPPH sample obeys the same law at temperatures above 150 K, but below this temperature a systematic deviation also occurs. Below 10 K the paramagnetism even decreases with decreasing temperature. The deviation is attributed to the pairing of electrons. In the solvent-free DPPH, less than 1 per cent of the unpaired electrons active at room temperature are left at 2.2 K.

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Samenvatting. - De statische magnetische susceptibiliteit van het organisch vrij radikaal  $\alpha, \alpha'$ -diphenyl- $\beta$ -picryl-hydrazyl (DPPH) werd gemeten volgens de Curie-methode. Het paramagnetisme van het specimen, waarin de vrije radicalen door gedeuteerde benzeenmolekulen gescheiden zijn, volgt de Brillouin functie voor niet-interagerende paramagnetische centra die elk een magnetisch moment hebben dat aan de spin van één enkel ongepaard elektron moet toegeschreven worden. Bij temperaturen beneden 4 K wordt er een systematische afwijking waargenomen. Het paramagnetisme van het onverdunde DPPH volgt ook voornoemde wet maar dan bij temperaturen boven 150 K. Beneden deze waarde treedt weer een systematische afwijking op. Beneden 10 K daalt het paramagnetisme met het dalen van de temperatuur. De afwijking wordt toegeschreven aan paarvorming van elektronen. In het onverdunde DPPH blijft minder dan een per cent van de elektronen, die bij kamertemperatuur magnetisch actief zijn, als ongepaarde elektronen over bij 2.2 K.

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Résumé. - La susceptibilité magnétique statique du radical libre organique  $\alpha, \alpha'$ -diphenyl- $\beta$ -picryl-hydrazyl, a été mesurée suivant la méthode de Curie. Le paramagnétisme de l'échantillon, dans lequel les radicaux libres sont séparés par des molécules de benzène deutérées, suit la loi de Brillouin pour des centres paramagnétiques non-interagissants dont chacun possède un moment magnétique dû au spin d'un seul électron non-apparié. A des températures inférieures à 4 K une déviation systématique est observée. Le paramagnétisme de l'échantillon DPPH non-dilué suit la même loi mais à des températures au-dessus de 150 K. Plus bas, la déviation systématique réapparaît. En dessous de 10 K le paramagnétisme décroît à température décroissante. La déviation de la loi est attribuée à la formation de paires d'électrons. Dans le DPPH non-dilué, moins de un pour cent des électrons, qui sont magnétiquement actifs à la température ambiante, reste comme électrons non-appariés à 2.2 K.

# ON THE PARAMAGNETISM OF DPPH

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## INTRODUCTION

As part of a study on the low-temperature properties of non-ionic organic free radicals, the static magnetic susceptibilities of  $\alpha,\alpha'$ -diphenyl- $\beta$ -picrylhydrazyl (DPPH) have been measured using the Faraday method [1]. Two extreme cases are considered : the first deals with a DPPH complex in which the radicals are separated by deuterated benzene, the second deals with a solvent-free DPPH sample [2]. Susceptibilities have been measured at temperatures between 2.2 and 300 K at six different fields. The nominal values of the strength of these fields are 20.6, 18.7, 14.7, 11.9, 9.0 and 6.1 kOe. They will be referred to by the subscript  $i$ , numbered from 1 to 6.

The reported experimental results are discussed from the point of view of electron pair formation.

## EXPERIMENTAL RESULTS

Part of the gramme susceptibilities of sample 1, what henceforth is called DPPH.C<sub>6</sub>D<sub>6</sub> is given in Fig. 1, as plotted by the computer [3]. The  $\chi_i$  values indicated by the + signs are  $\chi_1$ 's ; those given by the x signs  $\chi_6$ 's. Other data are omitted for clarity reason. The plot shows that the  $\chi$  values are strongly dependent on the reciprocal temperature. At higher temperatures they fit the equation :

$$\chi_i = \frac{A_i}{T} + C_i \quad (1)$$

The values of  $A_i$  and  $C_i$  are temperature independent. The first term on the right-hand side of equation (1) is the Curie law which expresses the behaviour of non-interacting paramagnetic centres. The temperature independent part is attributed to the susceptibility of the rest of the material. In the low-temperature region, a systematic deviation from the Curie law is observed. It seems that a saturation occurs in the magnetization, as expected from the Brillouin function. Consequently, the magnetization of sample 1 has been fitted to the Brillouin function,  $B(T,H)$  [4], for non-interacting paramagnetic centres each having a magnetic moment due to the spin only of a single unpaired electron. For each nominal field strength, a fitting was carried out using one single parameter :  $B_i$ , the free radical concentration, given by the ratio of the number of paramagnetic centres to the total number of formula units. The  $B_i$  values were chosen so that the values :

$$\chi_i = B_i \cdot \frac{B(T,H_i)}{H_i} + C_i \quad (2)$$

minimize, in the low-temperature region, the sum of the weighted squares of the deviations :

$$D = \sum_{n=1}^N [W \cdot (\chi_i - \chi_i')^2]_n \quad (3)$$

of the  $N$  measurements which have been taken at temperatures above 7 K. As the macroscopic magnetic moment is highest at the lower temperatures, the weighting factor  $W$  has been made proportional to the reciprocal temperature. The  $C_i$ 's are fitted values obtained from the susceptibility data taken at  $T > 100$  K. Indeed, at the higher temperatures the Curie term is lower, resulting in a better precision on the  $C_i$  values. In fact, the results have been obtained in an iterative process, where (i) the  $B_i$ 's are the fitting parameters in the low-temperature region using for  $C_i$  the values obtained from the high-temperature data, and (ii) the  $C_i$ 's, are the fitting parameters using a "most probable free radical concentration" as known  $B_i$  constants. The most probable free radical concentration is taken to be the average of the precedingly obtained  $B_i$  values, assuming that the concentration is equal for all six magnetic field strengths. The iterative process started with the theoretically expected values  $B_i = 1$  and  $C_i = \chi_d$ , the diamagnetic susceptibility of the substance. The diamagnetism of the sample has been estimated, from the data of Haberditzl [5] and Dorfman [6], to be  $\chi_d = -4.8 \times 10^{-7} \text{ emu.g}^{-1}$ .

The  $C_i$  values thus obtained deviate systematically from  $\chi_d$ , so that the presence of a saturated ferromagnetic impurity is supposed. The assumption is expressed by :

$$C_i' = \chi_d + \frac{K}{H_i} \quad (4)$$

in which  $\chi_d$  and  $K$  are constants and  $H_i$  is the magnetic field, the strength of which is indicated by the subscript  $i$ . The assumption requires an intermediate step in the fitting procedure. This step is carried out by choosing the value of  $K$  so that it minimizes the standard deviation :

$$s = \sqrt{\frac{\sum_{i=1}^6 (C_i - C_i')^2}{6-1}} \quad (5)$$

using for  $C_i$  the value obtained for  $C_i'$  in the preceding high-temperature fitting. The procedure finally yields the values given in Table 1.

TABLE 1

i	B <sub>i</sub>	C <sub>i</sub> × 10 <sup>7</sup>	C <sub>i</sub> ' × 10 <sup>7</sup>
1	0.973	- 5.6	- 4.4
2	0.976	- 4.1	- 4.3
3	0.978	- 3.1	- 4.2
4	0.976	- 3.2	- 4.0
5	0.987	- 4.7	- 3.8
6	0.979	- 3.1	- 3.3

The standard deviation (s) is  $0.9 \times 10^{-7}$  emu.g<sup>-1</sup> for  $K = 0.9 \times 10^{-3}$  emu Oe.g<sup>-1</sup>, and the most probable free radical concentration (B) is 0.978 (± 0.005). The relative deviations from the calculated values of the susceptibilities measured at 20.6 kOe using B and C<sub>i</sub>' in equation (2), namely :

$$\Delta = 100 \cdot (\chi_1 - \chi_1') / \chi_1' \quad (6)$$

are plotted in Fig. 2 versus the logarithm of temperature.

Susceptibility values of sample 2 (the solvent free DPPH) are given in Fig. 3. In the high-temperature region, the paramagnetism is practically identical to that of the preceding specimen. In the low-temperature region, however, the paramagnetism is strongly reduced in sample 2. The similarity in behaviour of the two samples at the higher temperatures justifies the similarity in the analysis of their data. For the solvent-free DPPH, the iterative process has also been started with the theoretical values  $B = 1$  and  $C_1' = \chi_d$ . The diamagnetism of the solvent-free DPPH is estimated to be  $- 4.5 \times 10^{-7}$  emu.g<sup>-1</sup>. The resulting values of C<sub>i</sub>', as obtained for  $T > 200$  K, are given in Table 2, column 3. Their corresponding B<sub>i</sub> values, as obtained in the temperature region between 150 and 300 K, are reported in column 2. The most probable free radical concentration in the solvent-free DPPH is  $B = 0.972$  (± 0.006). The relative deviations of the measured susceptibilities from those calculated (using B<sub>i</sub> = B and C<sub>i</sub>' = the average of the C<sub>i</sub>' values in equation (2)) are plotted versus log T in Fig. 4, for i = 1 (+ signs) and i = 6 (x signs).

TABLE 2

i	$B_i$	$C_i' \times 10^7$
1	0.963	- 4.8
2	0.970	- 4.5
3	0.979	- 4.0
4	0.977	- 4.1
5	0.975	- 4.2
6	0.969	- 4.5
average	0.972 ( $\pm 0.006$ )	- 4.3 ( $s=0.3$ )

## DISCUSSION

The magnetic susceptibilities of the  $\alpha$ ,  $\alpha'$ -diphenyl- $\beta$ -picryl-hydrazyl complex, in which the radicals are isolated from each other by deuterated benzene, fit the values expected from the Brillouin magnetization function for an unpaired electron concentration 0.978 ( $\pm 0.005$ ). The concentration, which is somewhat less than unity, can be explained on the assumption that the composition of the sample is not stoichiometric, i.e. that the benzene free radical ratio is not exactly 1. An indication supporting this assumption is that the composition of the sample is not very stable, as the specimen lost 0.6 % of its weight during two of the three days between preparation and installation in the apparatus (To prevent further escape of benzene, the sample was kept at temperatures below 175 K for the whole period of the susceptibility measurements. The treatment seems to have been effective, since no change in apparent susceptibility with time was observed).

The measured susceptibilities deviate from the values expected from the most probable unpaired electron concentration. The spread of the relative deviations, as given in the right-hand side of Fig. 2, is due to the scatter in the force determination. Indeed, at high temperatures, the force on the specimen is small compared to the force on the balance pan. The force ratio is  $3.2 \times 10^{-2}$  at 170 K, and at lower temperatures the force ratio is higher. From the point of view of force measurements, therefore, the precision of the susceptibility values should increase with decreasing temperature. In agreement with this reasoning is the spread of the deviations, which is found to be smaller on the left-hand side of Fig. 2. The mass of the sample,  $1.024 \times 10^{-4}$  g, was chosen to optimize the precision of the measurements in the low-temperature region. At temperatures below 6 K, however, the precision on the susceptibility values is limited mainly by the uncertainty of the temperature of the sample. On the basis

of superconductive transition temperatures as reference points, the sample temperature was estimated, in this low temperature region, to be known to  $\pm 0.01$  K [7]. Consequently, the systematic deviation from the Brillouin behaviour below 2.7 K, as observed in Fig. 2, is expected to be a real effect, and is attributed to the formation of pairs of radicals. This pair formation reduces the "high-temperature" unpaired electron concentration by 2 % at  $T = 2.2$  K.

Ferromagnetic impurities cannot always be avoided. If the field dependence of the magnetic susceptibility at the higher temperatures be attributed to iron, present in a not too dispersed form, one could calculate its mass concentration, because  $K$  is the ratio of the impurity to the sample-mass, multiplied by the magnetic moment of one gramme of the impurity [8]. This moment for bulk iron is  $221 \text{ dyn.cm.Oe}^{-1} \text{ g}^{-1}$ . The  $K$  value  $0.9 \times 10^{-3} \text{ emu.Oe.g}^{-1}$  results in about 4 parts per million of iron being sufficient to explain the field dependence. This explanation implies that a piece of  $4 \times 10^{-10}$  g of iron can still be representative for the bulk. This weight is considered to be the detection limit for iron in the DPPH sample, as the standard deviation  $s$  is of the same order of magnitude as the susceptibility differences between the  $C_1$  values, which suggests the presence of ferromagnetic impurities.

In contrast to the previously considered  $\text{DPPH.C}_6\text{D}_6$ , the composition of a solvent-free  $\alpha, \alpha'$ -diphenyl- $\beta$ -picryl-hydrazyl specimen is stable at room temperature. It has been possible, therefore, to measure susceptibilities up to 300 K and to observe that for  $T > 150$  K these susceptibilities also fit the values expected from the Brillouin magnetization function. The unpaired electron concentration in this case is 0.972 ( $\pm 0.006$ ). The 2.8 % deviation from unity may be due to the presence of unoxidized diamagnetic parent molecules. The stable organic-free radicals are generally difficult to prepare in pure form [9]. At lower temperatures the magnetization of the sample is less than the value expected from the Brillouin function with the "high-temperature" concentration of unpaired electrons. The absolute values of the relative deviations from this function, as plotted in Fig. 4, can be interpreted as the percentage of the "high-temperature" unpaired electron concentration, which has been eliminated by lowering the temperature to a certain value. One can speculate on the nature of the elimination of the unpaired electrons, for example, a free radical might react with a neighbouring one to form a molecule in a way similar to the chemical reaction of a hydrogen atom with another atom forming a diatomic molecule. In this model, 80 % of the "inert pairs" are formed in the rather extended temperature range between 35 K and 4.6 K. The width of the region might be attributed to a distribution of different configurations, for example, distances between neighbours. In favour of such a model is the observation that, in the solvent-



free DPPH, a 2 % reduction of the unpaired electron concentration occurs at about 100 K, whereas in DPPH.C<sub>6</sub>D<sub>6</sub> this percentage is only reached below 2.2 K. In the latter sample the distance between neighbouring free radicals is accepted to be larger, indicating that a difference in distance introduces a difference in the temperature at which the pairs are formed. To check this model, one should try to prepare samples in which the free radicals are localized more equi-distantly and then to look for a reduction in the "pair-formation" temperature region. In the measured sample, however, the smooth decrease of the unpaired electron concentration with decreasing temperature may be interpreted as an effect of the integration of a normal distribution of distances about the average for a single "distance population". Such a distribution mostly applies where some accidental errors are involved. Therefore, the effect may be interpreted as an indication of a random distribution of different distances in the sample. In such a model, the pairs should be formed randomly in the sample when the temperature is lowered. At very low temperatures, this model fails, since at 2.2 K only 1 % of the "high-temperature" unpaired electron concentration is still paramagnetically active. This is too low a figure for the model, since, in an "inert pair" system, the randomly formed molecules are expected to shield remaining unpaired electrons from each other. A lower limit for the remaining unpaired electron concentration is 3 %, a result from Monte-Carlo calculations [ 10 ]. Physical systems with a lower limit are imaginable, as discussed in [ 10 ] e.g. systems in which metal-like "fortuitous pairs" are formed or systems in which migration occurs.

#### CONCLUDING REMARKS

The static magnetic susceptibilities of the organic-free radical  $\alpha, \alpha'$ -diphenyl- $\beta$ -picryl-hydrazyl, can be attributed to two terms, a temperature dependent one due to the presence of unpaired electrons and a temperature independent one which is due to the diamagnetism of the molecule. At room temperature, the magnetization reveals the existence of roughly one unpaired electron per molecule. At lower temperature, however, the unpaired electron concentration becomes smaller and depends on the distance between the free radicals; this concentration decrease is attributed to pair formation. The model in which "inert pair" molecules are randomly formed must be discarded, at least below 3 K. The reason is that such molecules, in a random formation, would shield remaining unpaired electrons from each other, resulting in a lower limit of 3 % of the initially present unpaired electron concentration,

while, in the solvent-free DPPH, the remaining concentration is observed to drop below 1 %.

In the DPPH.C<sub>6</sub>D<sub>6</sub> sample, where the free radicals are isolated by deuterated benzene, the unpaired electron concentration reduction is observed at a much lower temperature than in the solvent-free sample. A stable specimen in which all free radicals were isolated by even larger diamagnetic molecules would be of interest for thermometry [11], as its magnetization is expected to follow precisely the Brillouin function.

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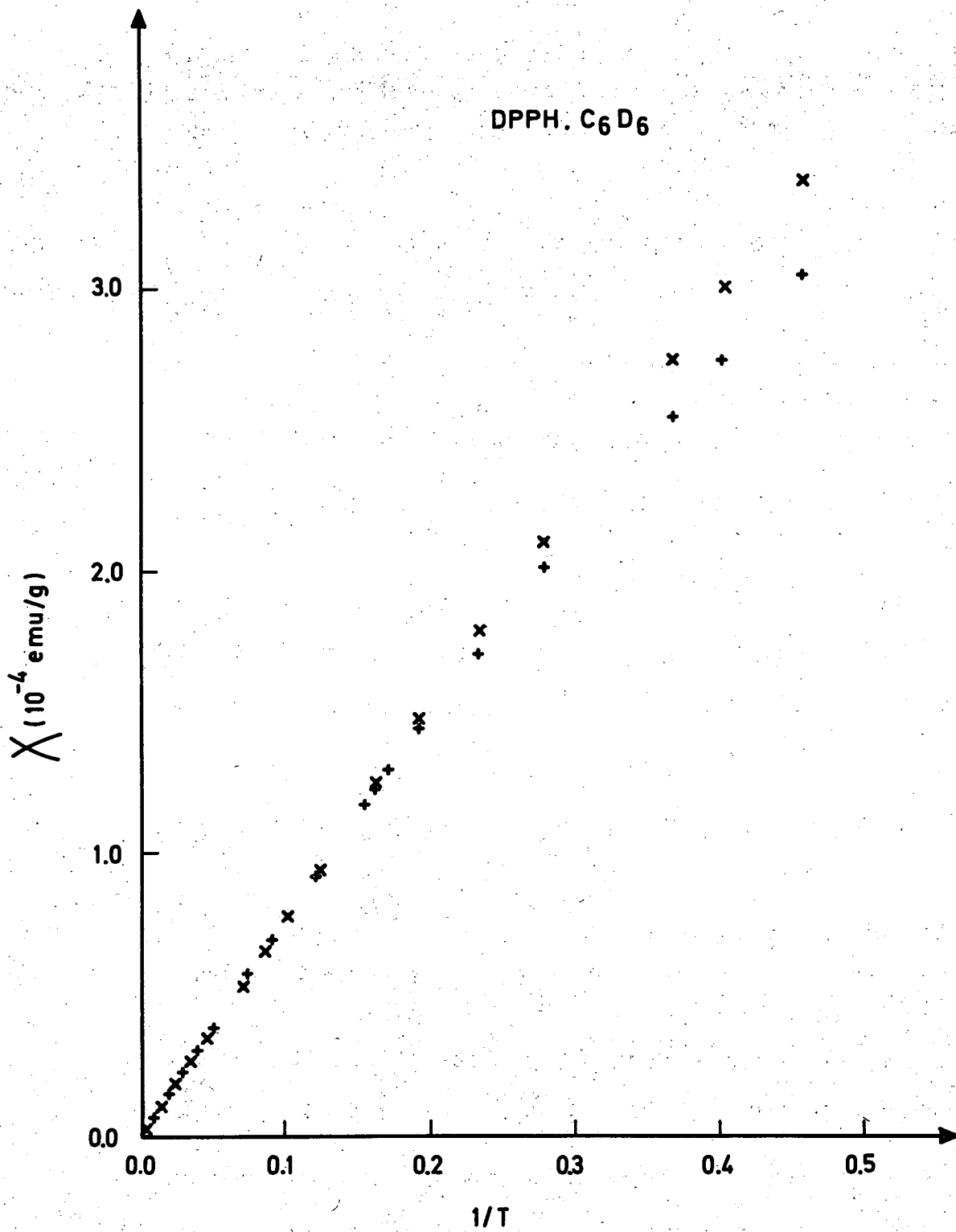


Fig. 1 : The magnetic susceptibility of DPPH.C<sub>6</sub>D<sub>6</sub>, measured at 20.6 (+) and 6.1 (x) kOe, versus reciprocal temperature

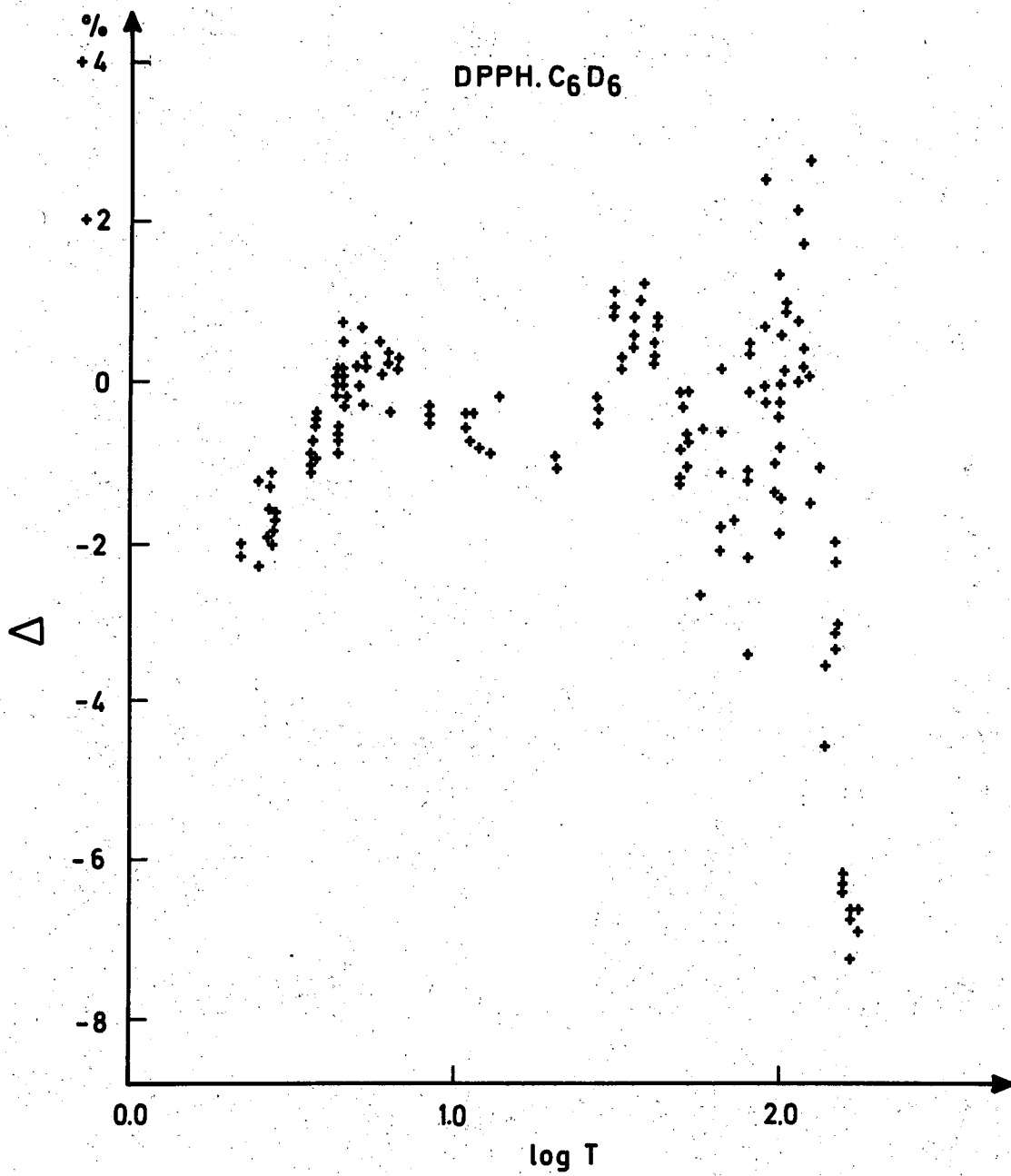


Fig. 2 : The proportional deviation of the measured magnetization from the Brillouin function versus the logarithm of temperature

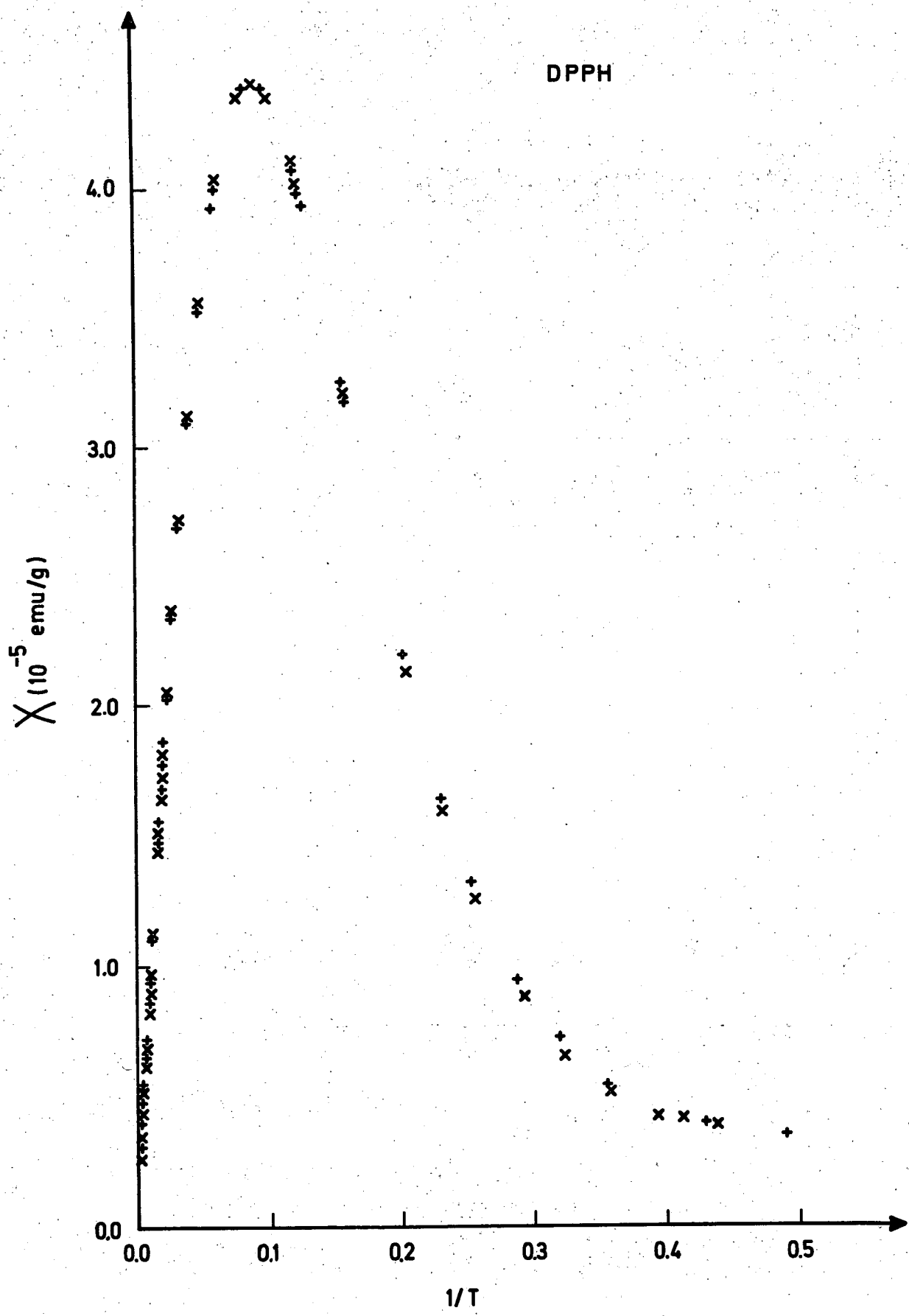


Fig. 3 : The magnetic susceptibility of solvent-free DPPH, measured at 20.6 (+) and 6.1 (x) kOe, versus reciprocal temperature

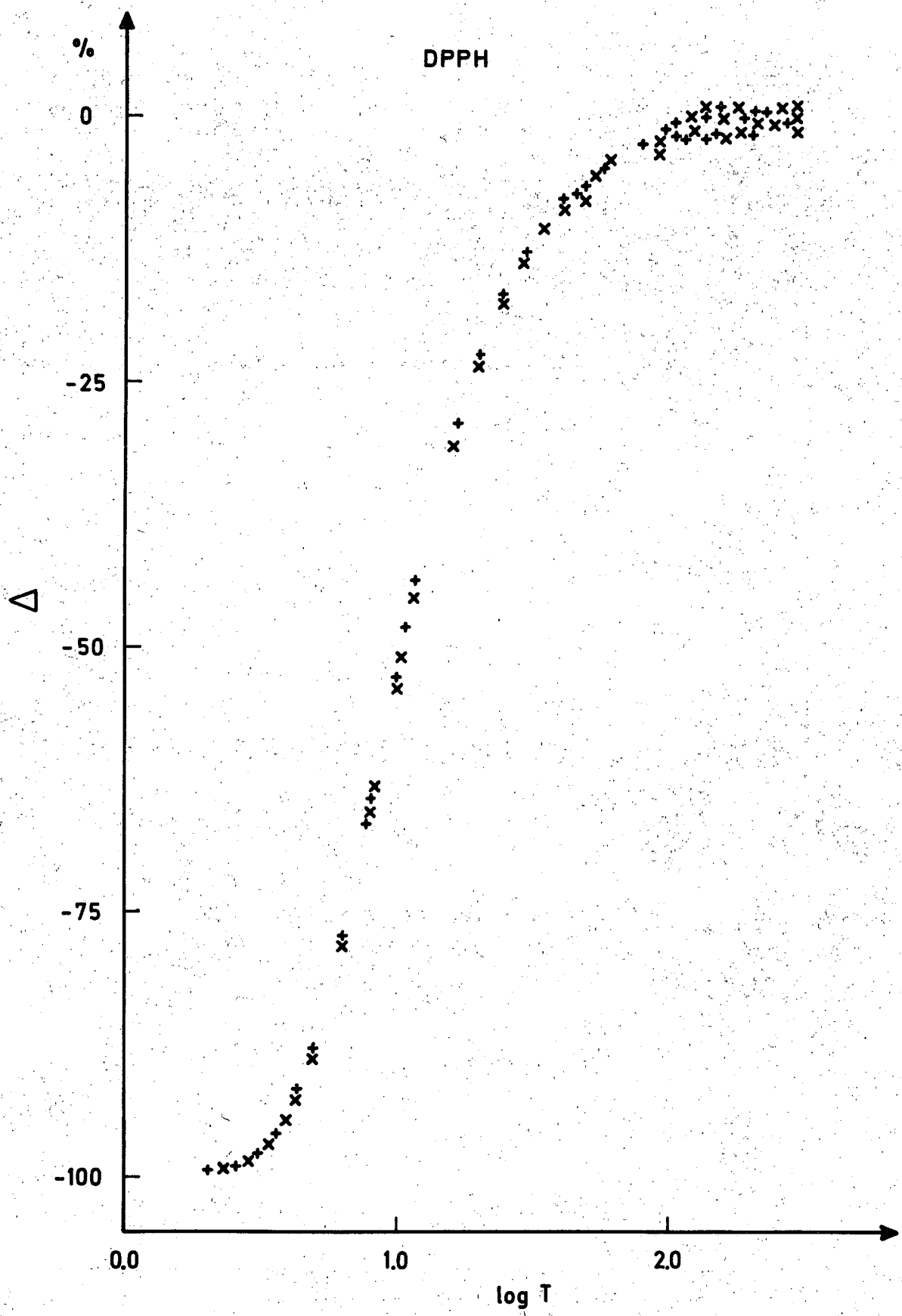


Fig. 4 : The proportional deviation of the measured magnetization from the Brillouin function versus the logarithm of temperature

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