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ANTIFERROMAGNETISM OF FREE RADICALS

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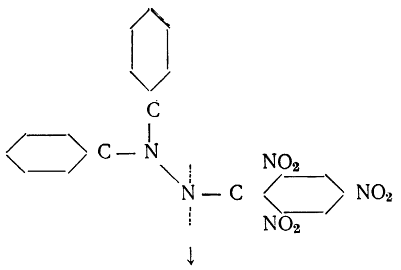
A transition to the antiferromagnetic state occurring between 0.2 and 0.3°K has been detected by the decrease in the integrated intensity of the electron paramagnetic resonance absorption line of the free radical α,α-diphenyl-β-picrylhydrazyl in a large single crystal (weight 25 mg) at a frequency of 42 Mc/sec.

In this paper the chemically stable organic free radical α,α-diphenyl-β-picrylhydrazyl (DPPH) is investigated. Its structural formula is shown below:



$(C_6H_5)_2N - NC_6H_2(NO_2)_3$

The magnetic properties of DPPH are caused by the presence in each molecule of an unpaired electron and are described by the spin Hamiltonian

$$\hat{\mathcal{H}} = \sum_{i>k} J_{ik}\hat{S}_i\hat{S}_k + g\beta H \sum_{i} \hat{S}_{z_i} + \hat{\mathcal{H}}_{\text{dip}}. \qquad (1)$$

The interactions in the Hamiltonian are written down in the order of decreasing magnitude. The first term corresponds to the exchange interaction of the unpaired electrons, the second to the Zeeman energy, which in our magnetic fields is less than the exchange energy, the third to the dipole spin-spin interaction. The z axis is chosen in the direction of the steady magnetic field H; β is the Bohr magneton; the spectroscopic splitting factor $g = 2.0036 \pm 0.0002$ at 300°K;[1] the spin $S = 1/2$.

We measured the electron paramagnetic resonance (EPR) spectrum of the free radical DPPH at a frequency of 42 Mc/sec in the temperature interval from 4.2 to 0.15°K. At temperatures below 1°K the integrated intensity of the EPR line is observed to decrease to zero. The disappearance of the resonance signal is explained by the reorganization of the energy spectrum of the system of magnetic moments of the unpaired electrons caused by their transition into an ordered antiferromagnetic state because of the presence of exchange interaction in the system.

The experimental results are presented as graphs in Figs. 1 and 2. They were obtained on three samples of DPPH crystallized from benzene solution: on two monocrystals weighing 25 and 13.7 mg and a crystalline powder weighing 50 mg. The structure of the monocrystals is monoclinic. The dimensions of the larger crystal were: thickness 2 mm, maximum linear dimension 5 mm. Cooling to 0.15°K was effected by adiabatic demagnetization of iron ammonium alum $FeNH_4(SO_4)_2 \cdot 12H_2O$. Reliable heat contact between the sample and the cold alum was achieved by means of a heat conductor, one end of which was pressed into the alum and the other end buried in the frozen drop of glycerine which enclosed the sample. The temperature was monitored by the paramagnetic susceptibility of the salt with an accuracy of 10%.

A 42 Mc/sec oscillator with the sample in its coil, was used to indicate the resonance absorption. The choice of low frequency was dictated by our desire to work with Zeeman splittings that were very much smaller than the exchange splittings.

To observe the resonance the steady magnetic field was modulated at 0.5 cps. The generator level, linearity of the spectrometer, and absence of saturation were all controlled, the last by means of the calibrator proposed by Pound.[2] The signal-to-noise ratio in work with the larger crystal was about 100. The absorption line was photographed on an oscilloscope screen.

The integrated intensity of the line s was taken as the product of the line width ΔH and the amplitude I of the absorption curve maximum and was expressed in relative units. This is strictly valid if the line shape does not change with temperature, since $s = k(I\Delta H)$, where $k \sim 1$ is a coefficient

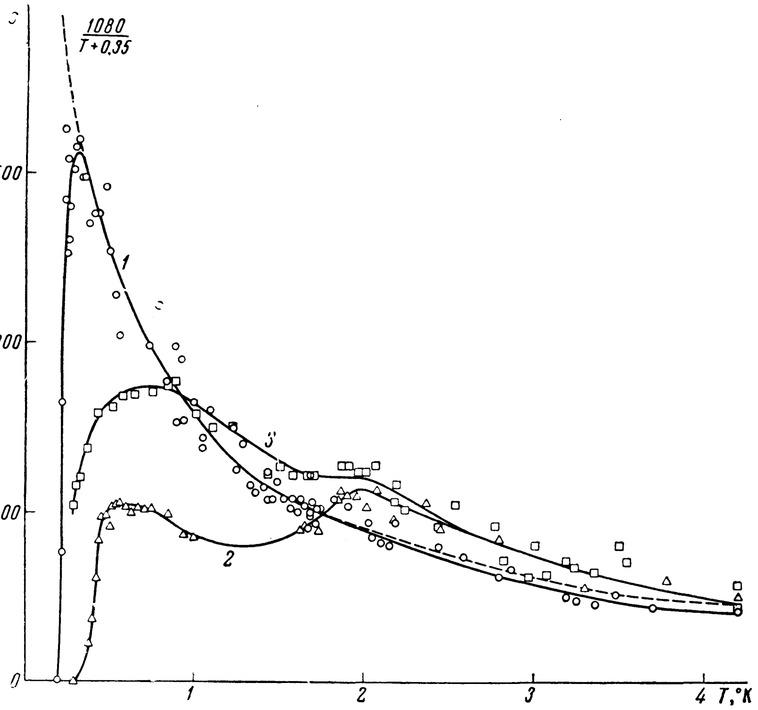


FIG. 1. Temperature dependence of the integrated intensity s of the EPR line (in relative units) of three DPPH samples: 1 – monocrystal weighing 25 mg, 2 – crystalline powder weighing 50 mg, and 3 – monocrystal weighing 13.7 mg. (Curves 2 and 3 have been corrected to a weight of 25 mg.)

that depends on the line shape. For Gaussian and Lorentzian curves—the actual shapes of absorption curves are usually intermediate to these—these coefficients are respectively equal to 0.94 and 0.64.

The most thorough work was done with the large monocrystal of DPPH weighing 25 mg. According to curve 1 in Fig. 1, the integrated intensity of the EPR line of this crystal follows the law $s = \text{const}/(T + \Theta)$ with $\Theta = 0.35$°K down to $T \sim 0.35$°K, and then it deviates from this law, abruptly falling and becoming equal to zero at ~ 0.18°K. The principal change in the integrated intensity occurs in the interval 0.2 to 0.3°K. The behavior of the curve does not depend on the orientation of the crystal relative to the constant magnetic field. The position of the maximum of the absorption curve does not depend on temperature within a precision of about 10%.

In the paramagnetic region the static susceptibility χ_0 of the radical is proportional to the area under the EPR line. Actually, according to the Hamiltonian (1) the imaginary part of the magnetic susceptibility $\chi''(\nu)$ has a single maximum about the frequency $\nu_0 = g\beta H/h$; consequently, the integrated intensity of the EPR absorption line

$$s = \int_0^\infty \chi''(\nu)\, d\nu.$$

From the Kramers-Kronig relation

$$\chi_0 = \chi'(0) = \frac{2}{\pi} \int_0^\infty \frac{\chi''(\nu)\, d\nu}{\nu} \tag{2}$$

it then follows that under the condition of a resonance line of width $\Delta\nu \ll \nu_0$ we have $\chi_0 \cong 2s/\pi\nu_0$. Thus the experimental dependence $s = \text{const}/(T + \Theta)$ is a simple expression of the Curie-Weiss law for the investigated sample. The temperature $\Theta = 0.35$°K has the meaning of the temperature limit of paramagnetism and is called the paramagnetic Curie point. It characterizes the magnitude of the exchange interactions in the system of unpaired spins, and the positive value obtained for Θ corresponds to the sign of the exchange integral that gives antiferromagnetic ordering.

The observed deviation from the Curie law below 0.35°K, consisting in a decrease in the integrated intensity of the EPR line of the radical, definitely indicates the occurrence in this temperature interval of a reorganization of the energy spectrum of the system involving a decrease in the number of particles possessing paramagnetic properties. This process takes place most intensely in the region 0.2—0.3°K. Hence it follows that the antiferromagnetic Curie point lies in this temperature interval.

It is to be noted that from our experiments it is impossible to obtain the dependence of the static susceptibility on temperature near the Curie point, since the method employed—EPR—sees in this region only the magnetic properties of a continuously decreasing part of the sample as it is cooled, that part which has a paramagnetic energy spectrum. In fact, near the Curie point $\chi''(\nu)$ depends on frequency in a manner otherwise than that predicted by the Hamiltonian (1), and consequently the intensity of the EPR signal s does not equal

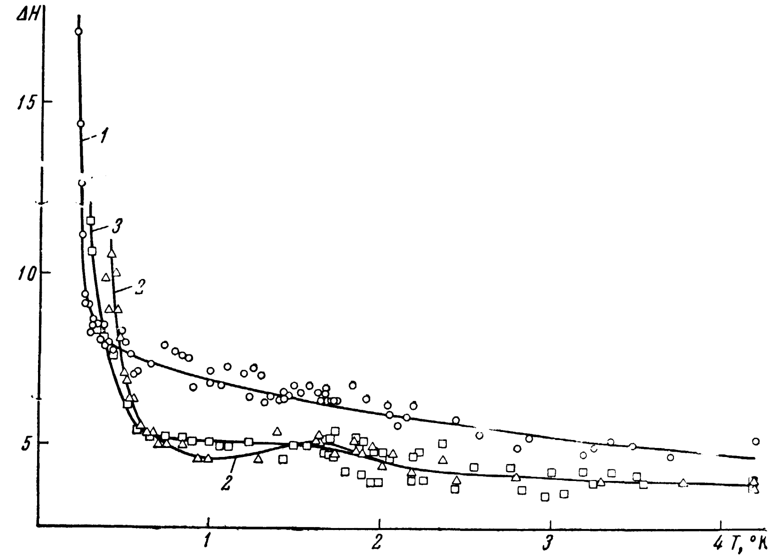


FIG. 2. Temperature dependence of the line width ΔH (in Oe) for the three DPPH samples; the curves are numbered as in Fig. 1.

the integral $\int_0^\infty \chi''(\nu)\,d\nu$ so that, according to Eq. (2) there is no well-defined connection between χ_0 and s.

There are reports in the literature on the measurement of the static susceptibility of DPPH in the paramagnetic region and on searches for the transition to the antiferromagnetic state. In 1933—1935, Katz and others[3] gave the value $\Theta \sim 10$—20°K. On the basis of these data the American authors of [4] undertook in 1953 to find the transition by the resonance method over the wide temperature region 300—2.5°K, but without success. In 1954 the Dutch authors of [5] investigated a crystalline powder of DPPH with the aim of searching for the antiferromagnetic state in the liquid helium range. They obtained $\Theta = 0.1$°K and found a slight decrease in $\chi_0(T+\Theta)$ in the interval 4.2—1.5°K. In 1960 J. Cohen (Grenoble University, France) measured χ_0 for a powder of DPPH in fields of ~ 1000 Oe at liquid hydrogen and helium temperatures and obtained $\Theta = 0.6$°K. All of these values for Θ have the same sign. The last value, considering the possible differences in the preparation of the radical, does not differ strongly from our value $\Theta = 0.35$°K.

The experimental results discussed above, relative to the magnitude of the exchange interaction in DPPH and the transition point are confirmed by an analysis of the experimentally determined temperature dependence of the EPR line width.

The temperature dependence of line width for the large crystal is given by curve 1 in Fig. 2. At T = 300°K, the line width (of a powder) is 1.75 ± 0.1 Oe, and at 77°K it is 1.5 ± 0.1 Oe. Curve 1 in Fig. 2 has two sharply differentiated temperature regions: a) a paramagnetic region ($T > 0.4$°K), with a gradual change in line width with temperature and b) the phase-transition region ($T < 0.4$°K), with rapid broadening.

In the paramagnetic region the EPR line width in DPPH is described by the theory of exchange narrowing of Anderson and Weiss,[6]

$$\Delta\nu = 2\langle\Delta\nu^2\rangle/\nu_k, \tag{3}$$

where the correlation frequency ν_k is a certain parameter in the theory,[6] proportional in the paramagnetic region to the exchange integral J of the Hamiltonian (1), and $\langle\Delta\nu^2\rangle$ is the second moment of the absorption line, calculated from the dipolar spin-spin Hamiltonian of [7]. Thus, knowledge of the line width gives information about the magnitude of the exchange interaction in the system.

The gradual change in width in the paramagnetic region can be explained by a gradual change in the exchange integral J. This can be correlated with a change in the crystalline lattice in this temperature region. In support of this is the increase in anisotropy of the g-factor at helium temperatures.[8] Since we do not know the detailed structure of the DPPH lattice, we shall made use of the relations for a simple cubic lattice with a lattice constant $l \sim 8 \times 10^{-8}$ cm for estimating the exchange integral J according to Eq. (3). On the basis of [6,7] we obtain for $S = 1/2$, $h\nu_k = 1.46\,J$ and $\langle\Delta\nu^2\rangle = 4 \times 10^{16}$ sec^{-2} = 4×10^4 Mc^2. Since, according to Eq. (1), the exchange interaction greatly exceeds the Zeeman energy in our case, then in accordance with [6] it is necessary to make the substitution $\langle\Delta\nu^2\rangle^* = {}^{10}/_3\langle\Delta\nu^2\rangle$ in Eq. (3). Carrying out the calculation, we get the tempera-

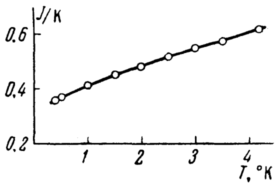


FIG. 3. Temperature dependence of the exchange integral in a crystal of the free radical DPPH.

ture dependence of J (see Fig. 3). The magnitudes obtained for the exchange integral J agree well with the magnitude of Θ found from measurements of the static susceptibility in the paramagnetic region.

We might mention that the verification of this change in J by the effect of the corresponding change in Θ on χ_0 is difficult, since χ_0 at T = 1—4°K is not sensitive to such small changes in Θ. The rapid increase in width in the transition region is apparently associated with the rapid change in the correlation frequency ν_k, which should decrease (while J stays the same) with the appearance of local magnetic ordering. It can be seen from Fig. 2 that the transition proceeds most intensely in the interval 0.2—0.3°K, which agrees with the conclusion drawn from the temperature behavior of the integrated intensity of the EPR absorption line.

The curve for the temperature dependence of the integrated intensity of the EPR line of the crystalline powder also indicates the presence of a phase transition. However, this transition begins at a higher temperature than in the case of the large crystal and proceeds in a more complicated fashion. It is possible that this is connected with a larger exchange interaction in the powder compared to the investigated crystal sample. In support of this is the fact that the powder has a narrower line in the paramagnetic region than the crystal. The curves for the small crystal (13.7 mg) take an intermediate position between the large crystal and the finely-divided crystalline powder. At present, we do not completely understand the difference in the results obtained for the large crystal and the small-crystal specimens. It is possible that it is connected with the specific method of preparing the molecular crystals of DPPH.

In conclusion, the authors express their sincere thanks to B. V. Ershov for his help in carrying out the experiments, B. N. Samoĭlov for making it possible for us to become acquainted with and gain experience in the technique of magnetic cooling in his laboratory.

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