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MAGNETIC PROPERTIES OF A CHAIN OF SPINS IN CRYSTALLINE FREE RADICALS

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The magnetic susceptibility of free iminoxyl radicals is isotropic and goes through a maximum with decrease of temperature. At low temperatures, ordering of the spin system by a magnetic field is observed. The magnetic properties of the radicals can be described completely by a one-dimensional Heisenberg model with isotropic antiferromagnetic interaction. The nature of the exchange interaction producing the chain of coupled spins is discussed.

INTRODUCTION

IN discussing the properties of antiferromagnetic dielectrics, the Heisenberg model is usually used for the exchange interaction between neighboring spins. However, there is no systematic theory for such a model since the ground state of the Heisenberg antiferromagnet is not known. The only exception is the linear spin chain, the wave functions of which were obtained by Bethe in 1931;[1] the energy of the ground state was calculated by Hulthén.[2] Also, although the problem of the isotropic Heisenberg chain is not as yet completely solved, we have sufficiently detailed information on its magnetic behavior. In the Hartree–Fock approximation the thermodynamic properties of such a chain have been calculated.[3,4] Griffiths calculated the magnetization curve of a spin chain at absolute zero temperature.[5] Bonner and Fisher performed an exact calculation for a finite number of spins forming a ring and then extrapolated these results to an infinite chain.[6]

These theories have not been subjected to detailed experimental confirmation because of the lack of appropriate substances. The well-known compounds $Cu(NH_3)_4SO_4$ and $CuKF_3$, in which there is likely to be a linear structure,[7,8] are not convenient substances since the former goes over to the antiferromagnetic state at low temperatures while the latter has too great an exchange integral. Earlier it was shown that the magnetic properties of crystalline free radicals are well described by the one-dimensional Heisenberg model.[9] It is of interest to study their properties in detail and compare them with exact calculations.

METHOD AND SAMPLES

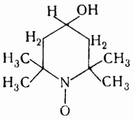
In order to observe ordering of a spin system by an external magnetic field the following condition must be satisfied:

$$H_{max}\mu > I \gg kT_{min}, \tag{1}$$

where H_{max} is the maximum value of the external field, μ is the magnetic moment of the atom or molecule, I is the exchange integral between nearest neighbors and T_{min} is the lowest temperature attained in the experiment. For crystalline free radicals the value of I oscillates from fractions of a degree to a few degrees and the condition (1) is fulfilled at very low temperatures and in magnetic fields of a few tens of kilo-Oersted.

The experimental setup satisfying these requirements is shown in Fig. 1. Very low temperatures were obtained by adiabatic demagnetization of iron-ammonium alum 13. The sample under investigation 5 was connected to the salt block by a copper conductor 9. The sample moment was measured by a ballistic galvanometer from the displacement of the sample in two coils 4 connected in opposition. Magnetic fields of intensity up to 30 kOe for the demagnetization and of intensity of up to 60 kOe for measuring the sample moment were produced by means of the superconducting solenoids 3 and 12. The temperature was determined from the susceptibility of a crystal of cerium magnesium nitrate 8.

Four iminoxyl radicals, having similar chemical structure, were investigated: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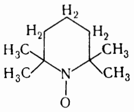
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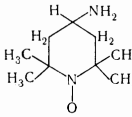
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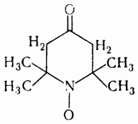

IV

These radicals are stable compounds. They were purified by repeated recrystallization in a vacuum at room temperature; monocrystals of weight up to 20 mg with good faceting also grew during this process and were also used in the experiment. Each radical molecule contains an unpaired electron whose g-factor is practically isotropic and close to the free electron g-factor.

RESULTS AND DISCUSSION

In spite of the similarity of the radicals, the interaction between the unpaired electrons of neighboring molecules differ considerably. Thus, for radicals I and IV the exchange integrals differ by two orders of magnitude. However, the general character of the temperature dependence of the magnetic susceptibility and of the dependence of the magnetic moment on the external field is essentially the same for all the radicals. The magnetic susceptibility goes through a maximum with decrease of temperature and remains constant as

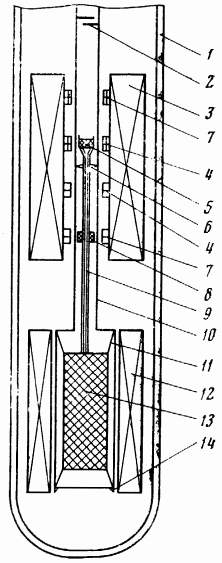


FIG. 1. Experimental setup: 1—Dewar vessel; 2—radiation screen; 3,12—solenoids; 4,7—measuring coils; 5—sample; 6—centering brace; 8—thermometer; 9—cold-conductor; 10—container; 11—caprone tension-wires; 13—salt for the demagnetization; 14—soft-solder joint.

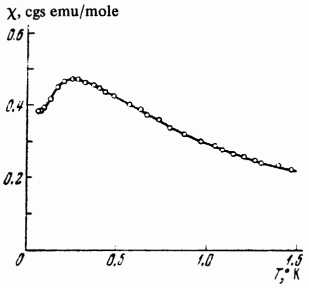


FIG. 2

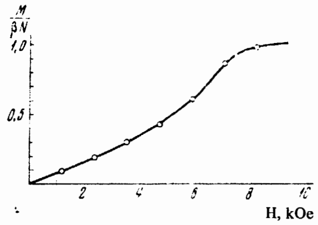


FIG. 3

FIG. 2. Temperature behavior of the susceptibility of radical III.

FIG. 3. Dependence of the magnetic moment of radical III on the field at T = 0.06°K.

T → 0 (Fig. 2). In sufficiently strong magnetic fields ordering of the spin system by the field occurs (Fig. 3).

The magnetic properties of free radicals can be described completely by the one-dimensional Heisenberg model with isotropic antiferromagnetic interaction. For such a model, in accordance with the calculations of Bonner and Fisher:[6]

$$I\chi_{max} / Ng^2\beta^2 \approx 0.07346, \qquad (2)$$

$$kT_{max} / I \approx 1.282, \qquad (3)$$

$$H_{cr} = 4I / g\beta, \qquad (4)$$

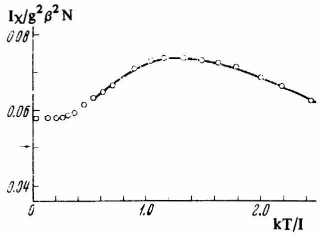
where χ_{max} is the maximum value of the magnetic susceptibility, which is attained at temperature T_{max}; H_{cr} is the value of the magnetic field corresponding to complete ordering of the spin system at T = 0.

In the table χ_{max}, T_{max} and H_{cr} for the four radicals investigated are given, along with the exchange integrals corresponding to these values. At temperatures $0 < T < I/k$ there is no phase transition in the field H_{cr}, the M(H) curve does not have a break and its form changes only in a small interval of fields close to the field H_{cr}. To determine H_{cr} it is convenient to make use of the relation[6]

$$M / M_{max} = 1 - A[1 - (H / H_{cr})]^{1/2}, \qquad (5)$$

which is correct for $H \to H_{cr}$. It is clear from the table that the exchange integrals found by three independent methods coincide within the limits of experimental error (the errors in determining χ_{max}, T_{max} and H_{cr} are not greater than 5%).

Parameter	Radical			
	I	II	III	IV
T_{max}, °K	5.3	2.4	0.29	0.048
I, 10^{-16} erg	5.70	2.59	0.312	0.052
χ_{max}, $\frac{\text{cgs emu}}{\text{mole}}$	$26.5 \cdot 10^{-3}$	$59.3 \cdot 10^{-3}$	$47 \cdot 10^{-2}$	2.86
I, 10^{-16} erg	5.75	2.57	0.324	0.053
H_{cr}, kOe	—	53	6.85	1.13
I, 10^{-16} erg	—	2.62	0.313	0.052



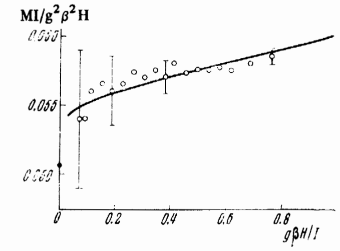


FIG. 4

FIG. 5

FIG. 4. Dependence on the reduced temperature of the reduced susceptibility of radical II.

FIG. 5. Curve for the magnetic susceptibility in weak fields of radical I, taken from paper [5].

In Fig. 4 is shown the temperature dependence of the magnetic susceptibility of radical II; the agreement between theory and experiment is very good. The susceptibility for temperatures $kT/I < 0.6$ was not calculated; however, the magnetization curve for a chain of spins at absolute zero is known.[5] At T = 0 the theoretical value of the susceptibility is given by: $I\chi_0/Ng^2\beta^2 = 0.05066$, which is markedly lower than our value of 0.058. This difference is connected with the fact that in weak fields the magnetic moment depends non-linearly on the field. To confirm this statement, the M(H) curve of radical I, which has the largest exchange integral, was plotted at the minimal temperature (Fig. 5). With decrease of the field, the error in the determination of the moment increases so that it is not possible to measure the susceptibility with sufficient accuracy. Thus no deviations of the magnetic properties of the free radicals from the accurately calculated properties of the one-dimensional spin chain were discovered.

In conclusion, we consider briefly the electron and crystal structure of the investigated iminoxyl radicals. The unpaired electron is basically localized on the nitrogen atom but there is also noticeable spin density on the oxygen atom bonded to it. The exchange interaction between the unpaired electrons of neighboring molecules occurs through this oxygen atom and the atoms bonded to the carbon in position four of the heterocycle of the neighboring molecule. This is confirmed by the fact that in the radicals studied replacement of these atoms changes appreciably the value of the exchange integral. The crystal structure of radical I is such that [10] neighboring molecules are bonded by a hydrogen bond in the manner indicated above and form linear chains. By the method of magnetic resonance it has been shown that there is significant spin density on the hydrogen atom forming the hydrogen bond.[11] We note also that the dipole-dipole interaction between neighboring molecules does not exceed 100 Oe which is substantially less than H_{cr} for all the radicals. Therefore, the existence of a chain of coupled spins in crystalline free radicals is completely natural.

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