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ON THE MAGNETIC SUSCEPTIBILITIES OF SOME IMINOXYL RADICALS

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Magnetic susceptibilities of organic stable radicals, derivatives of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl(TANOL), have been measured. The magnetic susceptibility of Ethyl-TANOL showing a broad maximum at a temperature of 0.17 K agrees well with the antiferromagnetic Heisenberg linear chain model, while that of Methyl-TANOL exhibits a characteristic feature of the three dimensional antiferromagnet.

The magnetic susceptibility of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TANOL) reported by Yamauchi, Ando, and the present authors (T. F., H. O. N., and Y. D.) has a broad maximum of susceptibility at about 6 K,[1)] a characteristic feature of a linear chain Heisenberg antiferromagnet predicted by Bonner and Fisher,[2)] while it was found that the magnetic susceptibilities of TANOL derivatives, Methyl- and Ethyl-TANOL (Figure 1) obey the Curie law at temperatures above 2 K, Weiss constants of both radicals being nearly equal to zero within the experimental errors.[3)] We wish to report here the magnetic susceptibilities of powdered Methyl-, and Ethyl-TANOL at temperatures below 1 K, and discuss the magnetic properties of Methyl-TANOL from its phenomenological aspect. These samples were prepared according to the procedure

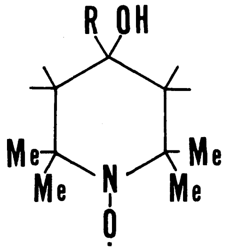
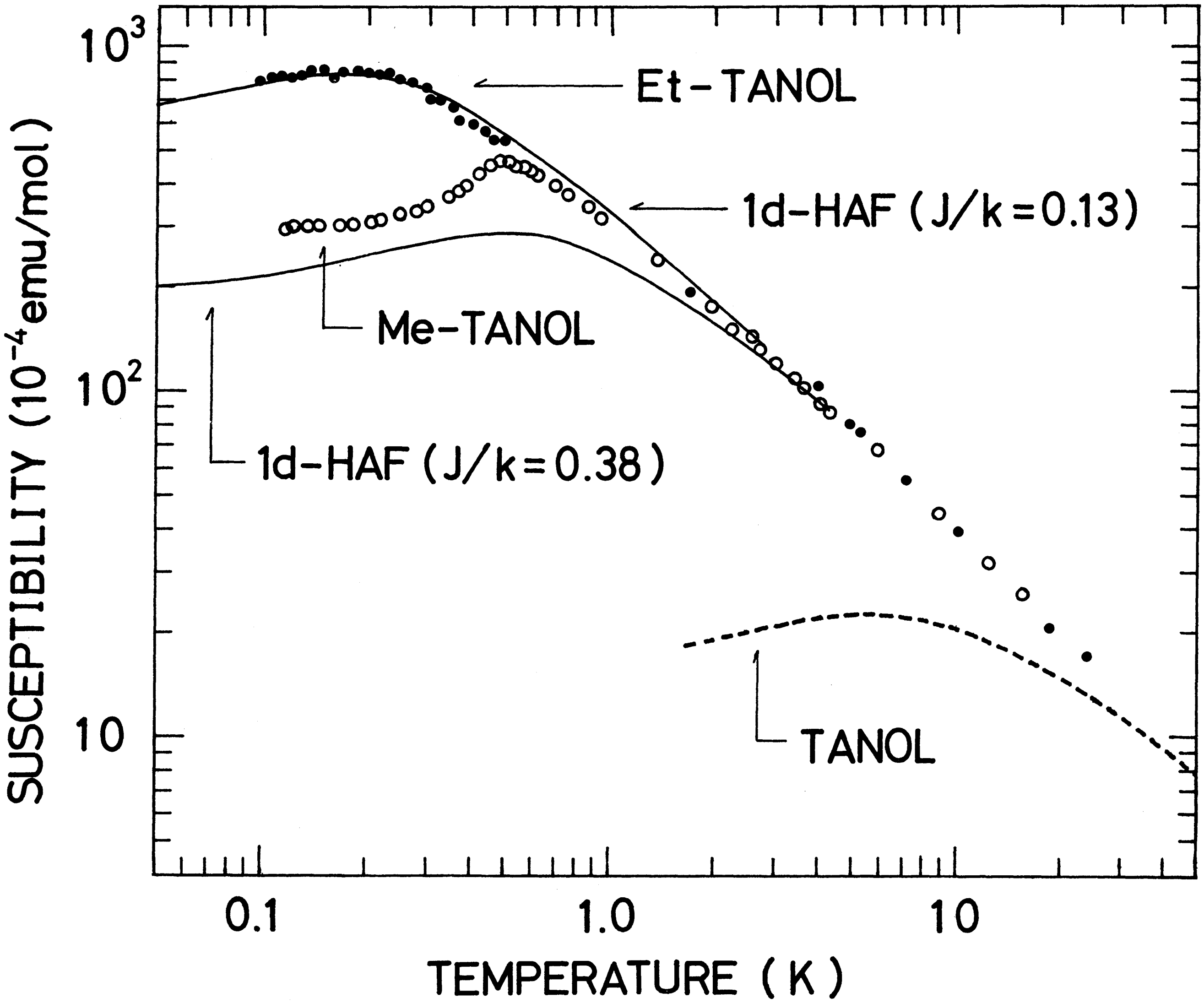


Figure 1. Constitutional formulae of the TANOL derivatives; R=H: TANOL, R=CH_3: Methyl-TANOL, and R=C_2H_5: Ethyl-TANOL.

of K. Watanabe, et al.[4)] The magnetic susceptibilities at temperatures below 1 K were measured by means of the adiabatic demagnetization cooling method. The radical concentrations of Methyl- and Ethyl-TANOL estimated from the susceptibility measurements at liquid nitrogen temperature are found to be 99.2, and 98.9%, respectively.

Ethyl-TANOL has a broad maximum of the susceptibility at 0.17 K, which is probably due to the short-range order effect in the electron spin systems coupled by the exchange interaction and the temperature dependence of the susceptibility shows a good agreement with the antiferromagnetic Heisenberg linear chain model predicted by Bonner and Fisher,[2)] assuming J/k=0.13 K as an exchange interaction constant. On the other hand, Methyl-TANOL has not shown a broad maximum of the susceptibility, but at 0.5 K its susceptibility reveals a peak (χ_{peak}) which cannot be predicted by the aforementioned model. Below the temperature where the peak appears, the susceptibility



falls off rapidly and reaches gradually the two-third of χ_{peak} with further decreasing temperatures, as is shown in Figure 2. As the behavior quite resembles that of the typical three dimensional antiferromagnet,$^{5)}$ we will be able to expect the occurrence of a magnetic phase transition at 0.5 K.

The magnetism of the organic free radical solids such as TANOL, BDPA, etc. with the preferred π-overlappings are well explained by the isotropic Heisenberg exchange interactions, perturbed by the exchange interactions with the other neighbor molecules which induce the magnetic phase transition.$^{6)}$Recent specific heat and proton magnetic resonance measurements below 1 K in the case of TANOL revealed that the magnetic phase transition occurs at about 0.4 K.$^{7)}$ Therefore, we are able to suppose from the magnetic susceptibility behavior of Methyl-TANOL that the methyl substitution to the TANOL molecule changes drastically the π-overlap between the nearest molecules in the c-axis direction which leads to the formation of a magnetic linear chain, and that the electron spins in Methyl-TANOL without any preferred π-overlapping interact magnetically rather in three-dimensional manner than in one-dimensional one. In order to examine the magnetic phase transition of Methyl-TANOL at the temperature 0.5 K, we are planning the EPR measurements at temperatures below 1 K.

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