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Metamagnetism in tanol suberate

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Résumé. — Les propriétés magnétiques statiques du radical libre nitroxyde subérate de tanol sont étudiées entre 0,05 K et la température ambiante. On a trouvé une transition métamagnétique à 0,38 K. Au-dessous de 0,38 K, les isothermes ont une forme en S, caractéristique des métamagnétiques. Aucun hystérésis en fonction du champ magnétique appliqué n'est observé jusqu'à la plus basse isotherme étudiée.

Abstract. — The magnetic properties of the free radical nitroxide tanol suberate have been studied between 0.05 K and room temperature. A metamagnetic transition has been found at 0.38 K. Below this temperature, the magnetization curves have the characteristic S-shape of metamagnets. No magnetic hysteresis has been observed down to the lowest temperature.

1. Introduction. — An antiferromagnet which possesses a field-induced transition to a ferromagnetic state is known as a metamagnet. This transition is characterized by an abrupt change from a low-moment state to a high-moment state, resulting in an S-shaped magnetization curve. This transition occurs at a field called the critical field H_c .

In the present study, we report detailed static magnetic investigations on a polycrystalline sample of tanol suberate, where a transition of the metamagnetic-type occurs. Based on preliminary results, this compound appeared to be ferromagnetic [1]. Tanol suberate is a free radical nitroxide; its chemical formula is $(C_{13}H_{23}O_2NO)_2$. Each molecule contains two free radicals N-O. One electron is localized on the N-O bonding [2]. Thus, the high temperature susceptibility obeys the Curie-Weiss law which is characteristic of localized spins.

2. Experimental. — Tanol suberate was prepared by the method indicated in [3]. The magnetic susceptibility is measured using a magnetic balance described in [4] in the range 4.2-300 K. Between 4.2 K and

10 K, the thermometer is a calibrated carbon resistor set close to the sample; for $T > 10$ K, a calibrated gold-cobalt-copper thermocouple is used.

The magnetization between 0.05 K and 4.2 K is measured by an induction method, the principle of which has been described in detail elsewhere [5]. The temperatures lower than 1.3 K are obtained by adiabatic demagnetization of a paramagnetic salt. For $T < 1.3$ K the thermometer is again a calibrated carbon resistor.

The calibration of the magnetization has been obtained by measuring the Curie constant C_M of the paramagnetic salt Gd_2SO_4 , $C_M = 15.66$ [6].

3. Results and discussion. — The field dependence of the molar magnetization is shown on figure 1 for several temperatures between 0.05 K and 4.2 K. Below 0.38 K, the magnetization isotherms have the S-shape characteristic of metamagnets. No hysteresis has been detected down to 0.05 K. The « critical » field H_c of the metamagnetic transition does not seem to vary very much with the temperature and is relatively small, $H_c \sim 100$ Oe, indicating that the antiferromagnetic interactions are quite low. The figure 1 shows the magnetization as a function of the internal field $H_{int} = H_{ext} - d.M$ where d is the demagnetizing factor. The transition is quite abrupt. Its small width may be due to the fact that the sample is not a single crystal and that therefore there exists a

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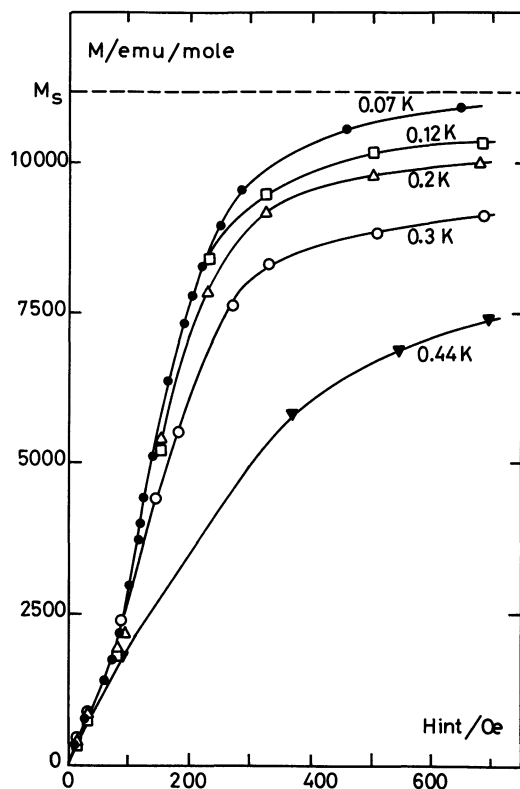


Fig. 1. — Magnetization as a function of the internal field of a powder of tanol suberate. Note the S-shaped character of the isotherms at 0.07 K, 0.12 K, 0.20 K and 0.30 K, indicating the metamagnetic behaviour.

distribution of critical fields H_c . The ratio M/H when measured in low fields displays a sharp maximum at 0.38 K (Fig. 2). At higher fields ($H \gtrsim 200$ Oe), this maximum disappears and the magnetization curves saturate, as shown in figure 3. This behaviour is similar to that found in the metamagnets MnAu_2 [8] and FeCl_2 [9]. A λ -type anomaly is also observed in the zero field specific heat at the same temperature [1].

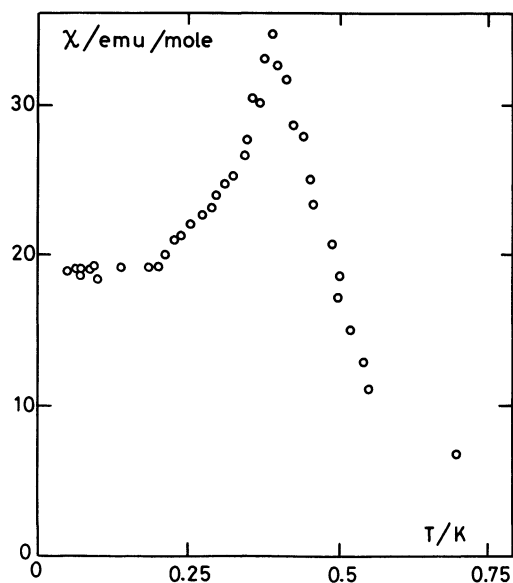


Fig. 2. — Low temperature molar susceptibility of tanol suberate.

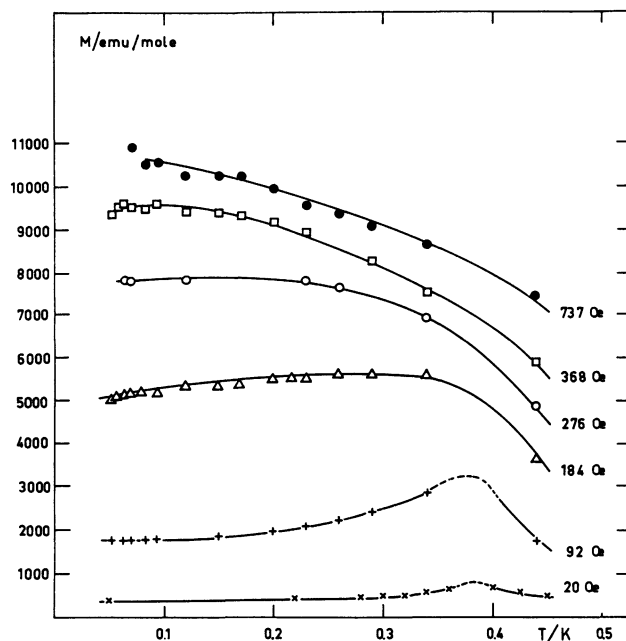


Fig. 3. — Molar magnetization vs. temperature for several values of the applied magnetic field. The metamagnetic behaviour is discernible from the presence of a peak in the curves at low field, but not at fields above 184 Oe.

In the paramagnetic region, the magnetic susceptibility is measured up to room temperature. Above 4.2 K, it is well represented by the Curie-Weiss law (Fig. 4); the molar Curie constant value C_M is $0.750 \text{ emu} \cdot \text{deg} \cdot \text{mole}^{-1}$ consistent with two independent spins $S = 1/2$ per molecule. The paramagnetic Curie temperature θ_p is positive and lies in the range of 1 K. A positive and low paramagnetic Curie temperature is consistent with the metamagnetic character of the compound. Below ≈ 5 K the reciprocal susceptibility vs. temperature strongly deviates from the Curie-Weiss law.

As shown by the crystallographic structure [10] (Fig. 5) the 1D-character is well established. So it is

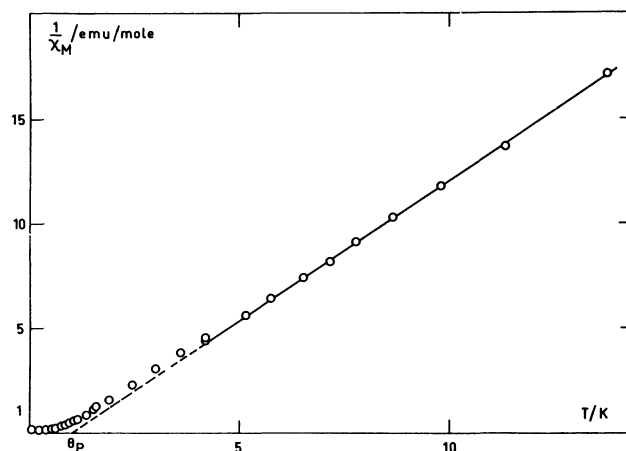


Fig. 4. — Reciprocal molar susceptibility of tanol suberate as a function of temperature. Well above the Néel point, the data follow the Curie-Weiss law, as shown by the straight line which corresponds to two uncoupled spins $S = 1/2$ per molecule.

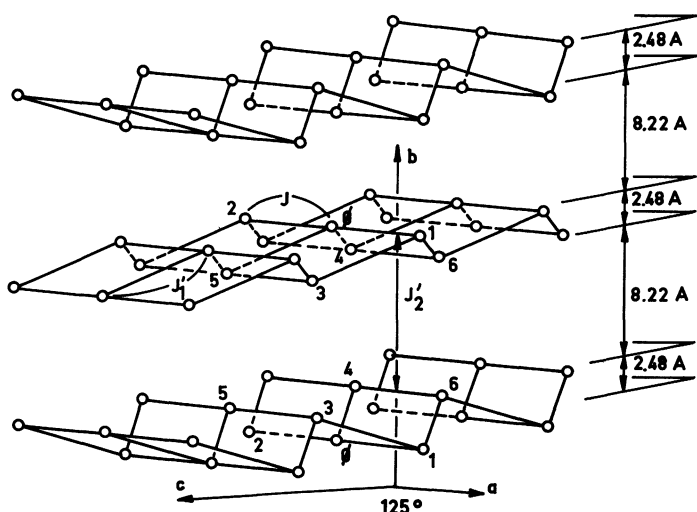


Fig. 5. — Sheet structure of the magnetic moments in tanol suberate (o symbolizes the middle of the NO group).

justified to examine the magnetic properties of the compound in a 1D-model. The intrachain Heisenberg Hamiltonian may be written as follows :

$$\mathcal{H} = -2J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$$

where the summation is taken over the nearest neighbour spins and J is the intrachain exchange coupling.

In such a model, if the intrachain exchange interaction J is positive, no maximum in χ is observed which does not agree with our results ; if J is negative, the maximum of χ occurs at a temperature 30 % greater than the maximum of the specific heat [11] which also contradicts our results. Thus, we have to assume the maximum of χ due to interchain interactions. In other words the magnetic order is tridimensional, which is well confirmed by the λ -type anomaly in the specific heat.

As we have done in a recent publication [12] it appears that the simplest way to analyse the susceptibility measurements is to assume that there are in tanol suberate interacting chains with a positive intrachain coupling J , then to apply a mean field correction to describe the other exchange interactions J' [14]. One may suppose the chains in the direction joining the nearest neighbours at a distance of 6.10 Å and the other interactions due to the significant neighbouring chains (two, z'_1 at 5.85 Å) or sheets (two, z'_2 at 8.22 Å) (see Fig. 5). The reduced susceptibility $(\chi_r)^{-1}$ for interacting chains may be written ⁽¹⁾ as follows :

$$(\chi_r)^{-1} = (\chi_{0,r})^{-1} - \lambda$$

where $(\chi_{0,r})^{-1}$ is the dimensionless reduced isolated chain susceptibility and λ is the mean field parameter

interaction : $\lambda = 2 z' \frac{J'}{J}$ where z' is the number of significant neighbours of a chain. The sign of λ determines the sign of J' . We follow the method indicated for ideal ferromagnetic chains to determine J but we compare the double log plot of the measured χ_M^{-1} vs. T with the double log plot of $(\chi_r)^{-1}$ vs. reduced temperature T/J , where λ is adjusted to obtain the best fit ; in this way, we may determine both J and the mean field correction.

The best fit is obtained for $J = 1.1$ K and for $\lambda = +0.2$. The mean interaction between the chains is then positive. Nevertheless, we have established that antiferromagnetic coupling exists between the chains. Thus we have to consider that two types of interchain interactions must exist : one, J'_1 , is positive, the other, J'_2 , is negative, and one has $|J'_2| < J'_1$ so that $J' \propto J'_1 + J'_2$ would be positive. Such an assumption is consistent with the crystallographic description. An estimation of J'_2 — the exchange interaction leading to the antiferromagnetic coupling — may be made from the critical field H_c of the metamagnetic transition using the approximate relation :

$$|J'_2| \sim g\mu_b H_c$$

$H_c \sim 100$ Oe leads to $|J'_2| \sim 0.015$ K.

A refined calculation of the mean field parameter gives

$$\lambda = 2 \left(\frac{z'_1 J'_1 + z'_2 J'_2}{J} \right)$$

with $z'_1 = z'_2 = 2$, one calculates $J'_1 \sim 0.070$ K. Theoretical studies [13], on the other hand, allow us to correlate J'_1 and J'_2 to J and T_c . Equations (40) and (44) of reference [13] lead to the relation :

$$\frac{T_c}{|J|} = S(S+1) \left/ \left[0.48 \left| \frac{J}{J'_1} \right|^{1/2} \left(1 + 0.253 \ln \left| \frac{J'_1}{J'_2} \right| \right) \right] \right.$$

The numerical factor 0.48 in this formula depends on the approximations. With the set of values $|J| = 1.1$ K, $|J'_1| = 0.07$ K and $|J'_2| = 0.015$ K one finds $T_N \simeq 0.28$ K in quite good agreement with the experimental value within the experimental errors and the theoretical approximations.

4. Conclusion. — Up to now, tanol suberate was generally considered as the first ferromagnetic purely organic compound. Our low temperature and low field measurements show it is in fact a metamagnetic. The interactions in the chain and between the first neighbours are positive, but a small negative interaction exists between the second neighbours. The low temperature magnetic ordering is therefore of 3D-character.

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⁽¹⁾ The method used is described in the article by Bonner J. C., *et al.* (Ref. [14]). The expressions of $(\chi_{0,r})^{-1}$ are given in the article by Swank D. D., Landee C. P. and Willett R. D. (Ref. [14] also).

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