Low-temperature Ferromagnetic Intermolecular Interactions between Galvinoxyl Radicals in Submicrocrystalline Solids

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Low-temperature magnetic properties with a positive θ of 4.4 K can be achieved in a powder of galvinoxyl radicals in pure form indicating short-range ferromagnetic intermolecular interactions between neighbouring spins.

The search for ferromagnetism in organic substances has been an active research area.[1] Among many stable radicals investigated for this purpose, the magnetic properties of galvinoxyl crystals (GAL, 1) were reported previously to exhibit a strong paramagnetism above 85 K with a positive Curie–Weiss temperature θ of 15 K.[2] Below 85 K a sharp undesirable magnetic transition going from a paramagnetic to a diamagnetic state was ascertained. This magnetic transition was altered by cocrystallization of galvinoxyl and its precursor of hydrogalvinoxyl in a certain ratio to exhibit an interesting magnetic behaviour at low temperatures with short-range ferromagnetic intermolecular interactions between these highly hindered radicals.[3,4]

Here, we report that the intrinsic paramagnetic to diamagnetic transition of galvinoxyl can be systematically suppressed in freeze-dried materials. The suppression allows us to realize a persistent paramagnetism in pure GAL radicals in a linear relationship to the Curie–Weiss law from 25 to 300 K with θ of positive 4.4 K. Galvinoxyls in the powder form were prepared by a freeze-dry technique at 5 °C using a highly dilute benzene solution of GAL in various concentrations. During the sample preparation, the benzene solution was filtered through Celite to remove any insoluble particles of Fe-related ferromagnetic impurities and then fully deoxygenated with nitrogen by freeze–pump–thaw cycles, prior to the solvent evaporation under vacuum, to prevent any partial loss of radicals. The radical concentration of the resulting finely divided brown powders of galvinoxyl was titrated according to the iodometrical method[5] using sodium iodide and sodium thiosulfate as reagents in sequence. Only samples with a nearly quantitative retention (100%) of the spin concentration were used for the study of their magnetic properties.

The static magnetic susceptibility and the magnetization between 2 and 300 K in a magnetic field of 6.2 kG were measured by using both Faraday balance and SQUID magnetometer. The magnetic susceptibilities (χ) were correc-

ted for the contribution of ferromagnetic impurities (less than 6 ppm of Fe equivalent) and for the diamagnetism, calculated to be $\chi_0 = -1.47 \times 10^{-3}$ cm^3 mol^{-1}. Fig. 1(a) shows the results of inverse magnetic susceptibility measurements for galvinoxyl crystals (as sample a) and freeze-dried samples b, c, d and e. Samples b–e were prepared from solution concentrations of 9.5×10^{-3}, 6.0×10^{-3}, 7.0×10^{-4} and 3.0×10^{-4} mol l^{-1} in benzene, respectively. The inverse magnetic susceptibilities of these materials (except for sample e) were found to follow approximately a linear Curie–Weiss relationship above 90 K prior to the onset temperature of diamagnetic transition. The Curie constant C_g for samples b, c, d (fitting between 90 and 300 K) and e (fitting between 25 and 300 K) were found to be 8.5×10^{-4}, 9.6×10^{-4}, 9.1×10^{-4} and 1.1×10^{-3}, respectively, which correspond to spin concentrations of 0.96, 1.08, 1.02 and 1.24 spins 1/2 per molecule, respectively. As a result, we observed clearly a systematic suppression of a paramagnetic to diamagnetic transition at an onset temperature of 82–85 K going from crystalline galvinoxyl sample a to powder sample e. Interestingly, by simply modifying the method of sample preparation, a sharp decrease of intensity of this transition from sample a to b was detected, as shown in Fig. 1(a). The trend appears to be correlated to the degree of molecular separation between galvinoxyl radicals by benzene
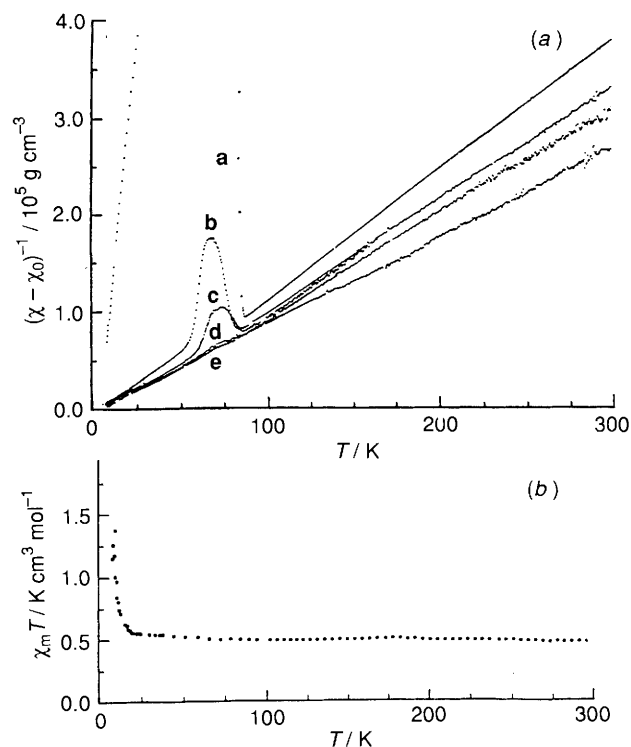

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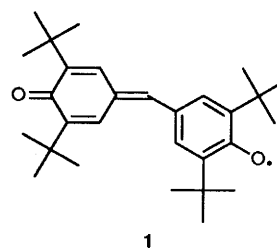
Fig. 1 Temperature dependence of (*a*) reciprocal magnetic susceptibilities, corrected for χ_0, $(\chi - \chi_0)^{-1}$, of galvinoxyl crystal **a** and GAL powder samples **b–e** prepared from highly dilute benzene solutions (see text) and (*b*) the temperature dependence of $\chi_m T$ plot of sample **e**
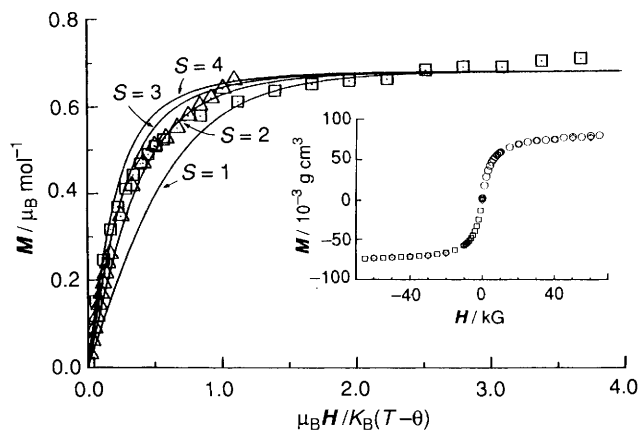

Fig. 2 Reduced magnetic field dependence of molar magnetization of a GAL radical powder sample **e** ($\square$: 1.3 K; $\triangle$: 4.2 K; the solid lines represent Brillouin functions) with the hysteresis plot in the insert

during the course of the freeze-dry process. That could, in principle, disturb the long-range order of molecular packing during the aggregation of molecules. Furthermore, the Curie–Weiss temperature θ, obtained from the fitting between 25 and 300 K, of sample **e** was found to be 4.4 K. The positive θ indicates that the intermolecular spin interactions in this powder-like solid are ferromagnetic in nature. The presence of this ferromagnetic intermolecular spin coupling can also be substantiated unambiguously in the temperature dependent plot [Fig. 1(*b*)] of the product of molar susceptibility (χ_m) and temperature (T). In this plot the value of $\chi_m T$ was found to be nearly constant as the temperature was lowered from 300 to 25 K, followed by a sharp increase below 25 K.

The study of spin multiplicity of sample **e** was carried out by the measurement of molar magnetization as a function of the reduced magnetic field as shown in Fig. 2. The magnetization isotherms up to 65 kG at 1.3 and 4.2 K were measured. A complete saturation on magnetization was observed in the magnetic field higher than 25 kG (1 G = 10^{-4} T) with a saturated magnetization of 8.0×10^{-2} G cm³ mol⁻¹. At 4.2 K the experimental magnetization isotherms ($\triangle$) showed a good agreement with the theoretical curves (solid lines) calculated from the Brillouin functions for magnetization with a spin state of $S = 3$ in the low magnetic field range and $S = 2$ in the high magnetic field range. These data suggest that the magnetization at low temperatures may arise from a short-range positive intermolecular spin exchange over four to six molecules on average. However, no hysteresis was observed in the plot of magnetization (M) *vs.* magnetic field (H) as depicted in the insert of Fig. 2.

To understand the difference in molecular packing among samples **a–e**, we investigated the structural correlation between galvinoxyl crystal and its powder analogue. Galvinoxyl radicals crystallized in a space group of $C2/c$-C_{2h}^6 (No. 15) with the monoclinic cell dimensions $a = 23.733(4)$, $b = 10.843(2)$, $c = 10.666(2)$ Å, $\beta = 106.64(2)°$, $V = 2630(1)$ Å³

and $Z = 4$ formula units [$D_c = 1.065$ g cm⁻³; $\mu\alpha$ (Cu-Kα) = 0.46 mm⁻¹]. The synchroton powder diffraction data were acquired utilizing the monochromatic X-rays ($\lambda = 1.5855$ Å) obtained by the use of a bent triangle Ge(111) crystal.† Intensity data were recorded in the vertical plane by step scanning at room temperature over a 2θ range of 7.5–62.5° in steps of 0.01. Surprisingly, the powder diffraction pattern [Fig. 3(*b*)] of sample **e** displays a close resemblance in peak positions (2θ) and the peak intensity below 25° to those of powder pattern [Fig. 3(*a*)] simulated from its single crystal parameters. From the width of the Bragg peaks measured, we estimated that the coherence length of the molecular order in the powder samples is at least larger than 600 Å. These patterns are indicative of a high degree of structural similarity between sample **e** and the macroscopic single crystal. Therefore, the curve-fitting analysis of the synchrotron powder pattern was executed utilizing the monoclinic cell parameters obtained from single crystal data as references. The Rietveld refinement of the synchrotron powder data was performed with the GSAS program. The atomic coordinates used for the single crystal model were fixed during the powder data refinement.‡ The thermal parameters of nonhydrogen atoms were refined as isotropic. The peak shape was approximately with a pseudo-Voight profile function. These structural parameters have been refined to convergence [R_p (unweighted) = 0.093] for all the observed data. The final value of refined monoclinic cell dimensions are $a = 23.705(3)$, $b = 10.863(1)$, $c = 10.650(1)$ Å and $\beta = 106.59°$. Fig. 3(*b*) shows the comparison between the calculated and observed powder diffraction profile of one galvinoxyl solid (sample **e**). Within the experimental limit, the powder sample **e** is confirmed to be, in fact, submicroscopically crystalline with structural parameters similar to those of galvinoxyl single crystal.

In conclusion, we found that the freeze-dry technique for the preparation of galvinoxyl solids leads to a significant alteration of their magnetic properties in terms of suppressing the molecular dimerization[2] at low temperatures in the solid

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† The powder diffraction data of samples in a beryllium cell were collected on Exxon beamline X10B at the National Synchrotron Light source, Brookhaven National Laboratory.

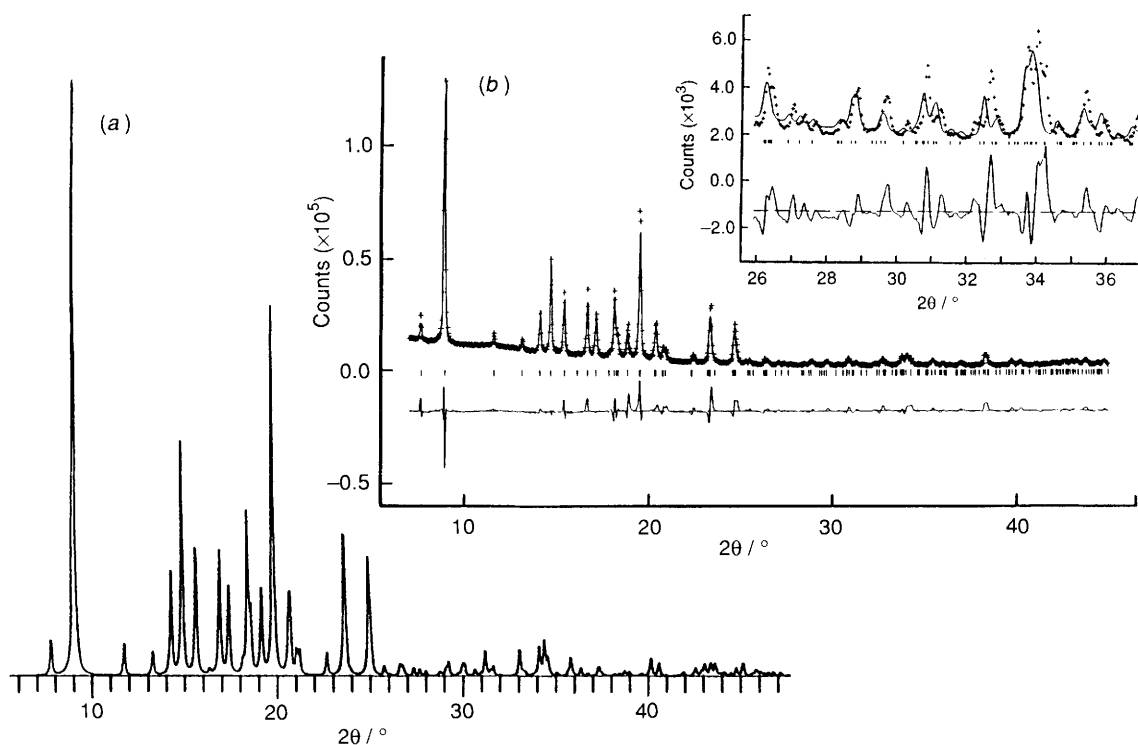‡ The attempt to refine the atomic coordinates for the compound **e** was not successful.

Fig. 3 (a) The powder pattern simulated from the single crystal parameters of sample **a** and (b) the calculated (solid line) and observed (+) synchrotron powder diffraction profile of a galvinoxyl radical powder sample **e**. The difference pattern (observed minus calculated) is shown below in the same scale as the observed pattern. Tick marks at the bottom line of the profile indicate peak positions. The expanded data beyond 25° are plotted in the insert.
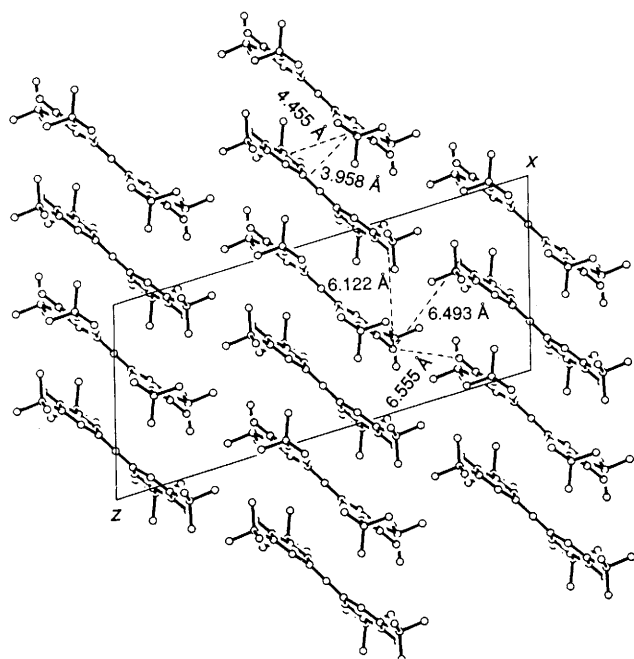

Fig. 4 Packing diagram of galvinoxyl radicals showing a perspective view of the molecular stacking arrangement along the z axis with several intermolecular distances

state. The structural analysis of these solids reveals that the change of structural parameters is minimum between single crystal and powders. One explanation could be given as the self-alignment of certain modifications of galvinoxyl mol-

ecular packing within the unit cell without causing a significant change of unit cell parameters. From the single crystal data the shortest distance between adjacent phenolic oxygen to oxygen atoms was found to be 6.122 Å along the molecular stacking z axes and 6.493 and 6.555 Å between two parallel molecular stacking z axes as shown in Fig. 4. The shortest distance from the centroid of one of the six-membered ring moieties of one galvinoxyl perpendicular to the CH=C moiety or to the closest centroid of the six-membered ring moiety of the adjacent molecule along the stacking direction is 3.958 or 4.455 Å, respectively. With this particular range of molecular separation, a small positional shift due to the molecular dislocation could induce an enormous effect on the nature of inter-molecular spin exchanges.

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