

# Molecular magnets $V(\text{tetracyanoethylene})_x \cdot y(\text{solvent})$ : Applications to magnetic shielding

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The specific advantages and limitations of a new class of polymer based magnets [exemplified by  $V(\text{TCNE})_x \cdot y(\text{solvent})$  (TCNE=tetracyanoethylene)] for static and low frequency magnetic shielding and inductive applications are evaluated using results of dc superconducting quantum interference device magnetization and ac permeability measurements. Present materials have very low density ( $\rho \sim 1 \text{ g/cm}^3$ ), relatively high resistivity ( $\sim 10^4 \Omega \text{ cm}$ ), and low power loss (as low as  $\sim 2 \text{ erg cm}^{-3} \text{ cycle}^{-1}$ ). The highest initial room temperature permeability observed to date (for solvent= $\text{CH}_2\text{Cl}_2$ ) of  $\mu_i = 13$  is modest for practical applications. Flexible processing methods are suggested for optimization of magnetic properties important for shielding applications.

Molecular based magnets present opportunities for developing a new class of lightweight materials for magnetic shielding and inductive applications, that are processible at room temperature using conventional organic chemistry. The field of molecular magnetism is in its infancy compared with other classes of soft magnetic materials. The discovery in the mid 1980's of ferromagnetism at 4.8 K in the linear chain electron transfer salt  $[\text{FeCp}_2^*][\text{TCNE}]$  (TCNE=tetracyanoethylene) marked the birth of molecular magnetism as a class of magnetic materials.<sup>1,2</sup> The report<sup>3</sup> in 1991 of room temperature ferrimagnetism in the polymeric material  $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  ( $x \sim 2, y \sim 0.5$ ) was the first indication that this class may be of technological use.

Magnetic shielding of low frequency magnetic fields is accomplished with soft magnetic materials.<sup>4</sup> Current soft magnetic materials suitable for magnetic shielding include transition metal alloys and ferrite ceramics.<sup>4</sup> Transition metal alloys may be tailored to have very high initial permeabilities ( $\mu_i \sim 20\,000$ ) and low coercive fields ( $H_c = 0.006 \text{ Oe}$ ) through choice of the transition metal concentrations, and annealing procedure to increase crystalline order. Cold working and machining reduce the shielding effectiveness of these materials to near that of high purity iron ( $\mu_i \sim 200$ ). Ferrite materials also require an anneal to reach their maximum permeabilities ( $\mu_i \sim 3000$ ).

Results of dc superconducting quantum interference device (SQUID) magnetization and ac permeability studies of  $V(\text{TCNE})_x \cdot y(\text{solvent})$  molecule based magnets are presented. The specific advantages and limitations of  $V(\text{TCNE})_x \cdot y(\text{solvent})$  and other molecular based magnets for static and low frequency magnetic shielding and inductive applications are identified. Although no members of this class are immediately suitable for these applications, their density, low power loss, and flexible low temperature processibility are promising for the development of lightweight shielding materials.

Samples of  $V(\text{TCNE})_x \cdot y(\text{solvent})$  are prepared by adding a solution of  $V(\text{C}_6\text{H}_6)_2$  in solvent X dropwise to a solution of TCNE in solvent Y, resulting in a black powder pre-

cipitate. Examples of solvents are: (i)  $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  ( $X=Y=\text{CH}_2\text{Cl}_2$ ); (ii)  $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN}/\text{C}_6\text{H}_6)$  ( $X=\text{C}_6\text{H}_6, Y=\text{CH}_3\text{CN}$ ); (iii)  $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$  ( $X=Y=\text{CH}_3\text{CN}$ ). IR spectra showed an absence of  $\text{C}_6\text{H}_6$  in the precipitate. Samples of V/TCNE based magnets also were prepared using an alternate procedure.<sup>5</sup> All samples are very reactive towards oxygen. Measurements were performed on powdered samples which were sealed under vacuum in quartz tubes. Elemental analyses yield significant uncertainties in  $x$  and  $y$ .<sup>3</sup>

The complex ac permeability was measured using the mutual inductance technique for  $10\text{--}10^4 \text{ Hz}$ .<sup>6</sup> The results presented in Fig. 1 were measured on powder samples at 400 Hz with an exciting field of 220 mOe. For  $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  (both preparations) and  $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN}/\text{C}_6\text{H}_6)$ , the permeability was measured by cooling to 2.0 K and stabilizing at each temperature before the ac permeability measurement. The ac permeability of

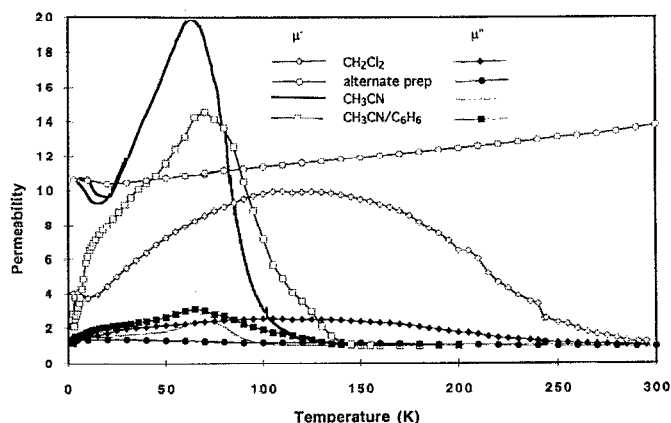


FIG. 1. Real and imaginary permeability of  $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ ,  $V(\text{TCNE})_x \cdot y(\text{alternate preparation})$ ,  $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN}/\text{C}_6\text{H}_6)$ , and  $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$ . Uncalibrated  $\chi'$  for  $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN}/\text{C}_6\text{H}_6)$ , and  $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  were previously published in Ref. 7.

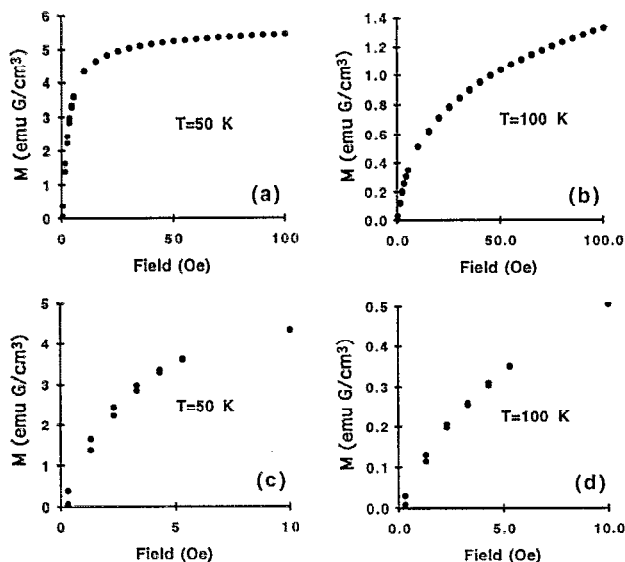


FIG. 2. Half hysteresis loops of  $V(TCNE)_x \cdot y(CH_3CN)$  at 50 K [(a) and (c)] and 100 K [(b) and (d)]. Lower figures [(c) and (d)] have expanded axes.

$V(TCNE)_x \cdot y(CH_3CN)$  was measured as the sample was cooled from 30 to 5 K at a rate of 0.5 K/min, and then held at 5 K for 2 min before sweeping up to 150 K at the same rate.

Magnetic hysteresis was measured at 50 and 100 K with a Quantum Design MPMS SQUID magnetometer by cooling in zero field from 150 K to the measurement temperature, and then measuring the magnetization as the field is ramped up to 100 Oe, down to  $-100$  Oe, and then back up to 100 Oe (at  $\sim 0.33$  Oe/s). The density of  $1.0 \pm 0.2$  g/cm<sup>3</sup> for both  $V(TCNE)_x \cdot y(CH_2Cl_2)$  and  $V(TCNE)_x \cdot y(CH_3CN)$  was determined in a glove box by pressing a pellet (1.3 cm diameter), and measuring its dimensions and mass. The demonstration shown in Fig. 3 was performed by suspending soft iron rods (common staples) above a  $SmCo_5$  permanent magnet [Fig. 3(a)], and then placing a pressed pellet (1.3 cm diameter) of  $V(TCNE)_x \cdot y(CH_2Cl_2)$  above the magnet [Fig. 3(b)] at room temperature under argon.

The ordering temperature  $T_c$  is above 350 K for  $V(TCNE)_x \cdot y(CH_2Cl_2)$ <sup>3,5</sup> (its decomposition temperature) 130–140 K for  $V(TCNE)_x \cdot y(CH_3CN/C_6H_6)$ ,<sup>7,8</sup> and 80–120 K for  $V(TCNE)_x \cdot y(CH_3CN)$  from both ac permeability and dc magnetization measurements. Initial permeability for  $V(TCNE)_x \cdot y(solvent)$  is independent of frequency from 10 Hz to 10 kHz, except near the spin glass freezing tempera-

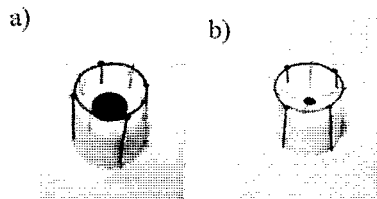


FIG. 3. (a) Folded soft iron rods (staples) are shown attracted to a  $SmCo_5$  permanent magnet. (b) With a pellet ( $r=6.5$  mm,  $t=1.7$  mm) of  $V(TCNE)_x \cdot y(CH_2Cl_2)$  at room temperature shielding the magnetic field, the soft iron rods hang freely.

ture  $T_f$  in  $V(TCNE)_x \cdot y(CH_3CN/C_6H_6)$  and  $V(TCNE)_x \cdot y(CH_3CN)$ , where strong frequency dependence is seen.<sup>9</sup> Microwave experiments at 6 GHz show very small ( $\sim 1$ ) initial permeability for  $V(TCNE)_x \cdot y(CH_2Cl_2)$  and  $V(TCNE)_x \cdot y(CH_3CN/C_6H_6)$  at all temperatures in this frequency range.<sup>10</sup> The real and imaginary parts of the 400 Hz ac permeability,  $\mu'$  and  $\mu''$ , Fig. 1, do not follow the dc magnetization curves<sup>7</sup> for these materials.

The  $\mu'$  indicated that the energy loss is greatest for  $V(TCNE)_x \cdot y(CH_3CN/C_6H_6)$ , and lowest for  $V(TCNE)_x \cdot y(CH_3CN)$ .  $V(TCNE)_x \cdot y(CH_3CN/C_6H_6)$  has a re-entrant spin glass phase below 10 K.<sup>7</sup> For  $V(TCNE)_x \cdot y(CH_3CN)$ , warming and cooling ac permeabilities, Fig. 1, show irreversibility below  $T_f \sim 18$  K.

The half hysteresis loops, Fig. 2, show low energy loss for  $V(TCNE)_x \cdot y(CH_3CN)$  of  $2$  erg cm<sup>-3</sup> cycle<sup>-1</sup> at 50 K and  $0.1$  erg cm<sup>-3</sup> cycle<sup>-1</sup> at 100 K. This compares favorably with the losses for technological materials presented in Table I. Room temperature hysteresis for  $V(TCNE)_x \cdot y(CH_2Cl_2)$  indicates a remanant magnetic induction  $4\pi M = 10$  G, coercive field 60 Oe, and hysteresis loss of  $5000$  erg cm<sup>-3</sup> cycle<sup>-1</sup>. The coercive field for an alternately prepared V/TCNE based magnet is two orders of magnitude lower.

Figure 4 presents the calculated static magnetic shielding factor,<sup>11</sup> defined as  $S = -20 \log(H_i/H_0)$ , where  $H_0$  is an applied static uniform magnetic field and  $H_i$  is the static magnetic field inside the sphere. Results are shown for a 10 cm outer radius spherical shield of mass 1 kg. Shielding factors  $S > 10$  are for materials that have undergone extensive purification and annealing treatments, which have not yet been developed for  $V(TCNE)_x \cdot y(solvent)$  based magnets.

Table I gives a comparison of present molecular magnets (including a variant prepared using solvent= $C_4H_8O$ <sup>11</sup>) with other magnetic materials used in shielding applications. Transition metal alloys offer high initial permeabilities ( $\mu_i$ ) and high saturation induction ( $B_s$ ), at the cost of having large densities ( $\rho_d$ ), large hysteresis losses ( $W$ ), and large eddy current losses caused by low resistivities ( $\rho_r$ ). Ferrite materials have smaller saturation induction and smaller initial permeabilities, but have lower eddy current and hysteresis power loss.  $V(TCNE)_x \cdot y(solvent)$  based magnets as yet have lower permeabilities [largest room temperature value to date being  $\mu_i = 13$  for  $V(TCNE)_x \cdot y(CH_2Cl_2)$ , Fig. 2] and low saturation induction, but have the advantage of being an order of magnitude less dense than transition metal materials and having low eddy current and hysteresis losses. For comparison,  $\mu_i$  for the linear chain molecular magnets [ $FeCp_2^*][TCNE]$ <sup>1</sup> and [ $CrCp_2^*][TCNE]$ <sup>13</sup> are 3.1 (4.7 K) and 3.6 (2.0 K), respectively, determined from their dc susceptibilities. With increases in permeability, molecular magnetic materials analogous to  $V(TCNE)_x \cdot y(solvent)$  can be applied to lightweight shielding of dc magnetic fields, and also to lightweight, low loss inductive applications such as transformer, inductor, and motor cores. Figure 3 demonstrates the effectiveness of  $V(TCNE)_x \cdot y(CH_2Cl_2)$  in attenuating the magnetic force exerted by a  $SmCo_5$  magnet on soft iron.

Though significant shielding is obtained for molecular based magnets such as  $V(TCNE)_x \cdot y(CH_3CN)$ , the effectiveness is much lower than that of currently used materials

TABLE I. Magnetic materials properties for shielding applications. Measurements are at room temperature, except where a footnote reference appears. Saturation induction ( $B_s$ ) for V/TCNE based magnets is taken at 100 G field, which represents induction outside of the hysteresis loop; saturation magnetization is much higher. MF and LF ferrites are MnZnFe ferrites for medium frequency (MF, 0.1–2 MHz) and low frequency (LF, <0.2 MHz) applications. Information from References 3, 4, 7, 13, and 16.

| Material   | $B_s$ (G)  | $B_r$ (G)                  | $H_c$ (Oe)                      | $\mu_i$                                    | $\mu_i/\rho_d$          | $\rho_r$ ( $\Omega$ cm) | $W$ (erg/cm <sup>3</sup> )   | $\rho_d$ (g/cm <sup>3</sup> ) |
|--|--|----------------------------|---------------------------------|--|-------------------------|-------------------------|------------------------------|-------------------------------|
| Fe (99.8%)   | 20 500   | 8600                       | 1.4                             | 10   | 1.3                     | $3 \times 10^{-5}$      | 30 000                       | 7.9                           |
| Fe (99.9%)   | 21 500   | ...                        | 1.0                             | 200  | 25                      | $1 \times 10^{-5}$      | 5000                         | 7.9                           |
| Fe (99.95%)  | 21 500   | ...                        | 0.05                            | 10 000                                     | 1300                    | $1 \times 10^{-5}$      | 5000                         | 7.9                           |
| Mumetal  | 6500   | 3000                       | 0.05                            | 20 000                                     | 2300                    | $6 \times 10^{-5}$      | 300                          | 8.7                           |
| MF Ferrite   | 4000   | 1500–2000                  | 0.05–1.2                        | 500–1000                                   | 100–200                 | $3.3 \times 10^6$       | 250                          | 5                             |
| LF Ferrite   | 3500–5000  | 800–1400                   | 0.12–0.38                       | 800–2500                                   | 160–500                 | 50–700                  | 45–130                       | 5                             |
| V(TCNE) <sub>x</sub> ·y(CH <sub>2</sub> Cl <sub>2</sub> )                  | 140 (320 <sup>b</sup> )<br>(315 <sup>a,b</sup> ) | 10<br>(19 <sup>a,c</sup> ) | 20–60,<br>(0.5 <sup>a,c</sup> ) | 2 (14 <sup>d</sup> )<br>(13 <sup>a</sup> ) | 2<br>(13 <sup>a</sup> ) | $1 \times 10^4$         | 5000<br>(13 <sup>a,c</sup> ) | ~1                            |
| V(TCNE) <sub>x</sub> ·y(C <sub>4</sub> H <sub>8</sub> O)                   | 210 <sup>b</sup>                                 | ...                        | ...                             | 10 <sup>e</sup>                            | ~10 <sup>e</sup>        | ...                     | ...                          | ~1                            |
| V(TCNE) <sub>x</sub> ·y(CH <sub>3</sub> CN/C <sub>6</sub> H <sub>6</sub> ) | 180 <sup>b</sup>                                 | ...                        | ...                             | 15 <sup>f</sup>                            | ~15 <sup>f</sup>        | $1 \times 10^5$         | ...                          | ~1                            |
| V(TCNE) <sub>x</sub> ·y(CH <sub>3</sub> CN)                                | 190 <sup>b</sup>                                 | 0.3 <sup>e</sup>           | 0.15 <sup>c</sup>               | 20 <sup>g</sup>                            | 20 <sup>g</sup>         | ...                     | 2 <sup>e</sup>               | ~1                            |

<sup>a</sup>Alternate preparation technique (Ref. 5); <sup>b</sup>20 K; <sup>c</sup>250 K; <sup>d</sup>150 K; <sup>e</sup>50 K; <sup>f</sup>75 K; <sup>g</sup>60 K.

( $\mu_i$  V(TCNE)<sub>x</sub>·y(CH<sub>3</sub>CN)  $\approx$  0.01  $\mu_i$  ferrite;  $\mu_i/\rho_d$  V(TCNE)<sub>x</sub>·y(CH<sub>3</sub>CN)  $\approx$  0.05  $\mu_i/\rho_d$  ferrite). Disorder may be added to V(TCNE)<sub>x</sub>·y(solvent) based magnets during preparation through the presence of additional reactants, present either as solvent or solute, creating molecular “alloy” materials. In V(TCNE)<sub>x</sub>·y(CH<sub>2</sub>Cl<sub>2</sub>), dichloromethane is suggested to be present primarily as a *spinless interstitial dopant*. As such, it will add disorder weakly to the exchange through superexchange and through van der Waals interactions with the unpaired-spin orbitals. It will also perturb the anisotropy by changing the local symmetry.

The role of acetonitrile in V(TCNE)<sub>x</sub>·y(CH<sub>3</sub>CN), and V(TCNE)<sub>x</sub>·y(CH<sub>3</sub>CN/C<sub>6</sub>H<sub>6</sub>) is much stronger, and is that of a *spinless substitutional* as well as *interstitial dopant*. Its effects on the exchange are through coordinating with the V, directly changing the occupancies of the unpaired-spin orbitals. Also,  $T_c$  is reduced through dilution. Replacement of a TCNE by an acetonitrile molecule breaks the local symme-

try, inducing random anisotropy.<sup>8</sup> Though the acetonitrile content cannot be measured accurately it is suggested that  $T_c$  is a measure of the relative concentration. Reduction of  $T_c \sim 140$  K in V(TCNE)<sub>x</sub>·y(CH<sub>3</sub>CN/C<sub>6</sub>H<sub>6</sub>) to  $T_c \sim 100$  K in V(TCNE)<sub>x</sub>·y(CH<sub>3</sub>CN) indicates that the level of “solvent doping” can be controlled by the relative concentration of reactants, both solvent and solute.

It is suggested that through the fabrication of high purity molecular magnet “alloys,” materials may be produced which are suitable for magnetic shielding and inductive applications at room temperature and above.

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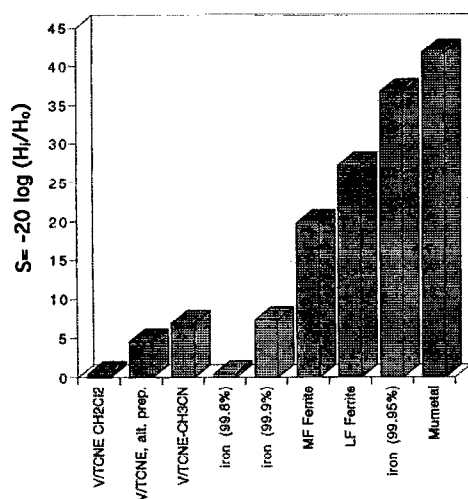


FIG. 4. Calculated magnetic shielding factor of various materials for a 1 kg spherical shield with a 10 cm outer radius. Values for ferrites, Fe (99.9%) and Mumetal are for materials that have undergone detailed annealing and purification processes to obtain high permeability. (Values from Ref. 3, 4, 7, and 13.)

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