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Disorder, exchange and magnetic anisotropy in the room-temperature molecular magnet V[TCNE]$_x$ – A theoretical study

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ABSTRACT

We report quantum chemical calculations to address yet unresolved and puzzling questions regarding the structural and magnetic disorder of V[TCNE]$_x$ (TCNE = tetracyanoethylene, $x \sim 2$), the first room-temperature molecule-based magnet. Starting from an ideal lattice model, containing TCNE ligands either tetra- or bi-connected to vanadium(II) ions, we identify the key sources of structural disorder, explaining the amorphousness and non-stoichiometric nature of V[TCNE]$_x$. The proposed model is prone to static disorder in terms of the bulk distribution of the tetra-connected TCNE species and to dynamic effects due to the relative rotational freedom of the bi-connected TCNE moieties. Density functional theory (DFT) calculations of the model system with rotated TCNE molecules show a rough energy landscape, consistent with the presence of magnetic irreversibilities in the system. The broken symmetry DFT approach evidences ferrimagnetic spin orientation for all TCNE configurations, ruling out the spin glass model. Multiconfigurational calculations with additional spin–orbit interaction allow for the account of the single-ion-anisotropy of the V(II) ions in different environments. We determine a small uniform zero-field-splitting ($D_c = -0.03$ K) of the bulk as well as a sizeable random anisotropy ($D_r = 0.56$ K) due to TCNE vacancies. We clarify the interplay of ferrimagnetism and random magnetic anisotropy in this system, which favours correlated sperimagnetic and not spin glass behaviour, in agreement with puzzling experimental data. Our approach goes beyond the material of interest here, as it can be applied to other disordered molecular magnets by correlating the sources of disorder with their effects on the magnetic properties.

1. Introduction

The recent discovery of spin injection in hybrid organic–inorganic spin valves [1] as well as in all-organic spin valves [2], and of spin-polarized transport in a light-emitting diode [3], all based on films of V[TCNE]$_x$ ($x \sim 2$, TCNE = tetracyanoethylene), has brought back to the front line the first room-temperature molecule-based magnet. The initial report [4] of a spontaneous moment at room temperature in the V[TCNE]$_x$·y(CH_2Cl_2) molecule-based magnet has stirred both astonishment and controversy with its amorphous and non-stoichiometric nature, as well as its subtle synthesis [5], revolutionizing the field of molecular magnetism [6,7].

Although the structure of V[TCNE]$_x$·y(CH_2Cl_2) has not been resolved experimentally, based on other experimental data it was proposed [4,5], that the oxidation state is V(II) and $x \sim 2$, such that the spins involved are 3/2 for the metal ion and 1/2 for the $[TCNE]^-$ radical anions. Important advances were made when V[TCNE]$_x$ films without any solvent were obtained by means of low-temperature chemical vapour deposition (CVD) [8,9]. Despite the faceted morphology, the films showed no X-ray lines, suggesting an amorphous structure, similar to the samples with solvent. X-ray Absorption Near-Edge Structure studies of CVD-prepared V[TCNE]$_x$ films concluded [10] that the vanadium ions are coordinated by about six nitrogen atoms, in a slightly distorted octahedral environment, and that there is strong binding between the V(II) ion and the nitrogen atoms of TCNE. An estimate of the vanadium oxidation state as V(II) also was obtained, in agreement with a V[TCNE]$_2$ stoichiometry [10]. Later on, an ultra high vacuum compatible in situ CVD process for deposition of V[TCNE]$_x$ films was developed and

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enabled the direct measurement of the occupied electronic structure [11,12].

Magnetic experimental studies of the V[TCNE]$_x$·y(S) systems (with S being acetonitrile or tetrahydrofuran) revealed [13,14] static critical behaviour consistent with existing models for random anisotropy magnets (RAM), previously applied only for site-diluted and amorphous metallic alloys [15]. It was speculated that the magnetic disorder was due to the structural and substitutional disorder resulting from the incorporation of the spinless solvent, as well as the random coordination topologies of the vanadium ions [13,14]. Similar scaling studies performed for other members of the family M[TCNE]$_x$·y(CH_2Cl_2), with M = Mn, and Fe, showed a very rich magnetic behaviour for both compounds, with double-transition random anisotropy characteristics for the Fe-based system [16] and re-entrant spin-glass behaviour for the Mn-based material [17]. More recently, photoinduced magnetization studies emphasized [18] the light-induced increase of random magnetic anisotropy due to increased structural disorder.

To date, little theoretical work has been done on the structure and electronic properties of the V[TCNE]$_x$ system. Recently, a model structure was proposed [19] and on that basis the structural, electronic, and magnetic properties were investigated using density functional theory (DFT) with periodic boundary conditions (PBC). However, to date, disorder and anisotropy have not been studied theoretically for V[TCNE]$_x$. Despite piling experimental evidence indicating random anisotropy and not spin glass behaviour, no theoretical explanation has been provided so far.

We explore here possible sources of structural disorder and analyze their impact on the magnetic properties of the system. By means of DFT calculations we determine the strength and sign of the exchange coupling constants and are able to explain both why irreversibilities are present and why the spin glass/random exchange model is not applicable. Furthermore, based on multi-configurational methods, considering the additional spin–orbit interaction, and on in house routines for the numerical differentiation of the energy, containing the Zeeman interaction due to an external magnetic field, we can determine the uniform as well as the random single-ion-anisotropy of the V(II) ions. We show that our results explain the experimental data, clarifying the interplay of ferrimagnetism and random magnetic anisotropy in V[TCNE]$_x$ and indicating correlated sperimagnetic and not spin glass behaviour.

2. Background on pure and disordered magnets

The exchange coupling constant $\mathcal{J}$, for a system of two electrons is related to the difference between the energies of the two possible spin configurations (parallel and antiparallel). The result is an effective interaction, in the spin space, described by the Heisenberg exchange Hamiltonian [6]:

$$\hat{H}_H = -2\mathcal{J}S_i \cdot S_j \tag{1}$$

The ferromagnetic state, characterized by parallel alignment of the spins, occurs when the exchange constant, $\mathcal{J}$, is positive, whereas the antiferromagnetic state, characterized by antiparallel spin alignment, arises when the exchange integral is negative.

The single-ion anisotropy (SIA) arises if the symmetry of the environment is lower than cubic. In second order of perturbation theory, the additional spin–orbit (SO) interaction leads to a zero-field splitting matrix which has different elements, even in the diagonal form. In the diagonal basis one gets a spin Hamiltonian that describes the single-ion-anisotropy [20,21]:

$$\hat{H}_{SIA} = D\left(S_z^2 - \frac{1}{3}S(S+1)\right) + E(S_x^2 - S_y^2) \tag{2}$$

In the case of axially symmetric environments $E = 0$ and the single-ion anisotropy is just [20] $\hat{H}_{SIA} = DS_z^2$.

This contribution to the spin Hamiltonian expresses the fact that in the absence of an applied magnetic field the spins tend to orient along preferential directions, induced by the anisotropic environment through the crystal field. We note that in most practical cases for transition-metal ions some distortions from the ideal symmetry are present causing some anisotropy to arise [21]. The single-ion anisotropy constant, D, is proportional to the square of the SO coupling constant (which has typical values of 10^2 cm^{-1}) and inverse proportional to the crystal field splitting ($\sim 10^4$ cm^{-1}) being of the order of 1 cm^{-1} or even smaller for many transition metal ion systems [20,21].

When combined with the Heisenberg exchange, the SIA can favour, in its two limiting cases, either Ising ($D \to -\infty$) or XY ($D \to \infty$) anisotropy of the spin systems. While a Heisenberg spin is isotropic (one can picture the classical image of a vector that can point anywhere on a sphere) and has a spin-dimensionality of $n = 3$, an XY spin can point anywhere on a circle ($n = 2$), and an Ising spin can point along a single given direction either up or down ($n = 1$) [7,22].

Disorder can be quenched or annealed [7,23–25]. In the case of random magnets, the disorder is quenched if the spatial distribution of exchange is frozen in, due to fixed magnetic moments. Disorder is considered annealed if the magnetic ions can diffuse in the solid and change the distribution of exchange. The two types of disorder are distinct and lead to very different types of magnetic behaviour.

The main feature of the dynamic behaviour of systems with disorder is the slower rate of relaxation processes. In ordered macroscopic systems the thermodynamic equilibrium is regained very quickly after the perturbation is removed such that for normal experimental times, even at phase transitions when the relaxation times are the largest, one can ignore nonequilibrium effects [25]. In random systems the relaxation is hindered by disorder and the evolution back to equilibrium is slower [25].

A magnetic system is frustrated if it cannot minimize the energy of each spin pair in the network, simultaneously [26]. The strength of the frustration is characterized by the number of configurations that minimize the total energy equally well. Frustration is generated by the competition between interactions of different kinds (e.g., competing ferro- and antiferromagnetic interactions or competing nearest-neighbor and next-nearest-neighbor interactions) or by the topology of the lattice (e.g., triangular, kagomé, pyrochlore lattices with antiferromagnetic nearest-neighbor interactions, etc.) [27]. A simple diagram classifying disordered magnets based on frustration and degree of disorder is shown in Fig. 1.

The dilute magnets [25,28] are systems with random exchange but with no frustration. From a theoretical point of view, the dilute ferromagnet, can be modeled by a random exchange coupling, such that the interaction varies only in strength, but not in sign. The equilibrium behaviour of dilute ferromagnets is qualitatively the same as that of pure systems [25], the subtle effects of disorder

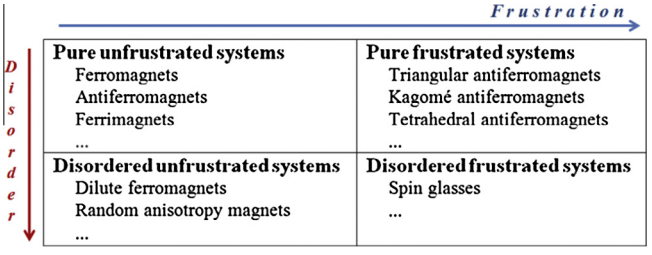

Fig. 1. Diagram illustrating a classification of disordered magnets based on frustration and the degree of disorder. For details see Refs. [7,27].