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Field Induced versus Local Anisotropy in Single Ion Magnets

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The aim of this paper is to compare the anisotropies in a system containing isolated magnetic centers produced by two independent effects. The first one is the interaction of an otherwise isotropic ion with the external magnetic, giving rise to the field induced anisotropy. The other one is due to the local interaction with the ligand field known as the zero field splitting. Integer and half integer spins are considered. Field induced anisotropy is of the easy-plane character and, under the constraint of $g\mu_{\rm B}SH = D$, it is inferior to that due to zero field splitting except for the case of the half integer spin at the lowest temperatures. At high temperature the anisotropy vanishes independent of the spin parity as expected.

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1. Introduction

Magnetic anisotropy is one of the technologically promising features of molecular magnets. On the one hand, it directly affects the size of the barrier to reversal of magnetization which is a determining factor in whether the magnetic species, such as a single-molecule or single-ion magnet [1, 2], may be used as the smallest component of data storage. On the other hand, it provides the playground for engineers willing to construct directionally programmable sensors. Hence, the widespread quest for new materials exhibiting strongly anisotropic magnetic properties. In the case of single-ion magnets the magnetic anisotropy arises from a specific configuration of the ligand field and is known as the zero-field splitting [3], because it occurs in the absence of the external magnetic field. On the other hand, the applied magnetic field itself does introduce the anisotropy in the otherwise isotropic media of paramagnetic pure spin carriers. Hence, a natural question arises how these two types of magnetic anisotropies, i.e., field induced anisotropy (FIA) on a pure-spin ion or zero field splitting (ZFS) anisotropy on a single-ion species, compare between themselves. To the best of our knowledge this issue has not been tackled yet. The present communication addresses this problem drawing extensively on the results obtained in [4], where both types of anisotropies for ions with spin of 1, 3/2, 2, and 5/2 were discussed. On the one hand, the need for such considerations is strongly implied by the developments in the field of coordination chemistry [5–7], in general, and in that of isolated polynuclear d- or f-electronic systems displaying substantial magnetic anisotropies [8–13], in particular. On the other hand, we know of no experimental setup dedicated to measuring the field induced anisotropy nor the issue is addressed in the otherwise comprehensive reviews [14, 15].

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2. Results

The approach adopted in this work is to present the temperature dependence of the magnetic susceptibilities and the corresponding anisotropies for two cases, i.e., where the anisotropy is purely field induced (FIA) or exclusively due to the zero-field splitting (ZFS). The model systems will involve an instance of the ion with integer ($S = 1$) and half integer ($S = 3/2$) spin. In order to enable the comparison between the different situations reduced temperatures t_H and t_D will be defined, i.e., dimensionless measures of temperature normalized with respect to the characteristic energy scales of both effects.

2.1. Field induced anisotropy

Let us consider the interaction of localized magnetic moments with the external magnetic field H assumed, without loss of generality, to be aligned along the z axis. The corresponding reduced temperature is defined as:

$$t_H = \frac{k_{\rm B}T}{\mu H}, \tag{1}$$

where $k_{\rm B}$ is the Boltzmann constant, $\mu = g\mu_{\rm B}S$ is the magnetic moment corresponding to spin S, g denotes the spectroscopic Landé factor, and $\mu_{\rm B}$ — the Bohr magneton. The corresponding susceptibility tensor is then diagonal $\chi = \mathrm{diag}\left(\chi_\perp, \chi_\perp, \chi_\parallel\right)$ and its components read

$$\chi_\perp(S, t_H) = \frac{N_{\rm A}\mu^2}{k_{\rm B}T} w_1(t_H), \tag{2}$$

$$\chi_\parallel(S, t_H) = \frac{N_{\rm A}\mu^2}{k_{\rm B}T}\Big(w_1(t_H) + w_2(S, t_H)\Big), \tag{3}$$

where $N_{\rm A}$ is the Avogadro number (molar quantities are considered) and

$$w_1(t) = tB_S(t),$$

$$w_2(S,t) = \frac{S+1}{S} - \frac{1}{S}\coth\left(\frac{1}{2St}\right) B_S(t)$$

$$-tB_S(t) - B_S^2(t) \tag{4}$$

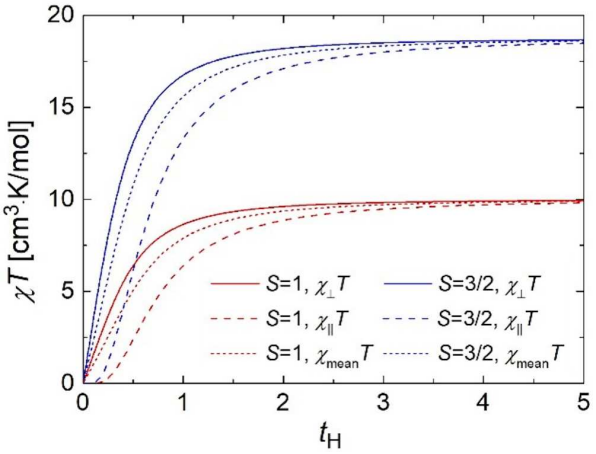

Fig. 1. Temperature dependence of the diagonal components of the susceptibility tensor, given in Eqs. (2) and (3), for spin values $S = 1$ (red), and $3/2$ (blue), corresponding to the case of anisotropy induced by applied field $\boldsymbol{H} = [0, 0, H]$.

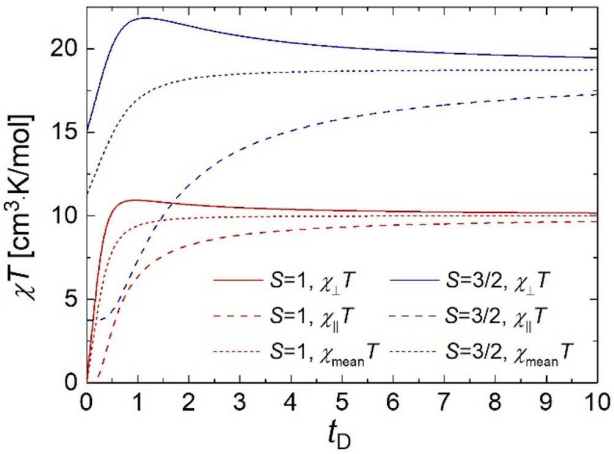

Fig. 2. Temperature dependence of the diagonal components of the susceptibility tensor, given in Eqs. (6)–(9), for spin values $S = 1$ (red), and $3/2$ (blue), corresponding to the case of ZFS anisotropy with a positive axial parameter $D > 0$.

with $B_S(t)$ being the Brillouin function. Figure 1 shows the temperature dependence of the susceptibility tensor components together with the mean value of the susceptibility χ_{mean}, calculated as one third of the susceptibility tensor trace. Two spin values are considered $S = 1$ and $S = 3/2$ with the Landé factor $g = 2$. It is apparent that independent of the spin value the field induced anisotropy is of the easy-plane character with $\chi_\perp > \chi_\parallel$ for all temperature values.

2.2. Zero field splitting

Let us consider the local anisotropy of the spin S ion due to the zero field splitting effect. For the sake of comparison only the axial ZFS parameter D is assumed to be nonzero and positive ($D > 0$), which is known to give rise to the easy-plane anisotropy. Moreover, let us assume that the spectroscopic tensor $\mathbf{g} = \text{diag}(2, 2, 2)$. The corresponding reduced temperature pertinent to this case reads

$$t_D = \frac{k_\text{B} T}{D}. \tag{5}$$

In this case the susceptibility tensor is similarly diagonal $\chi = \text{diag}(\chi_\perp, \chi_\perp, \chi_\parallel)$ with the corresponding components given by the formulae

$$\chi_\perp(S = 1, t_D) = \frac{8 N_\text{A} \mu_\text{B}^2}{k_\text{B} T} \frac{\exp(1/t_D) - 1}{\exp(1/t_D) + 2} t_D, \tag{6}$$

$$\chi_\parallel(S = 1, t_D) = \frac{8 N_\text{A} \mu_\text{B}^2}{k_\text{B} T} \frac{1}{\exp(1/t_D) + 2}, \tag{7}$$

for $S = 1$, and for $S = 3/2$ by

$$\chi_\perp(S = 3/2, t_D) = \frac{4 N_\text{A} \mu_\text{B}^2}{k_\text{B} T} \frac{1}{2} \left(1 + \tanh(1/t_D) + \frac{3}{2} t_D \tanh(1/t_D)\right), \tag{8}$$

$$\chi_\parallel(S = 3/2, t_D) = \frac{4 N_\text{A} \mu_\text{B}^2}{k_\text{B} T} \left(\frac{5}{4} - \tanh(1/t_D)\right). \tag{9}$$

Figure 2 shows the temperature dependence of the susceptibility tensor components together with the mean value of the susceptibility χ_{mean} for both spin values.

2.3. Comparison of FIA and ZFS effects

For the sake of comparison of the anisotropy effects in the cases of FIA and ZFS let us define a measure of the anisotropy based on the susceptibility tensor components

$$a = \frac{\chi_\perp - \chi_\parallel}{\chi_{\text{mean}}}. \tag{10}$$

The thus defined anisotropy parameter a is dimensionless and positive for the easy-plane type of magnetic anisotropy, where $\chi_\perp > \chi_\parallel$. The temperature dependences of parameter a calculated in the FIA and ZFS cases for $S = 1$ and $3/2$ spin values are depicted in Fig. 3. The plot assumes the equality $t_H = t_D = t$. Let us note that there is a nontrivial scaling factor between t_H and t_D, i.e. $t_H = f\, t_D$, where $f = D/(\mu H)$. The condition $t_H = t_D = t$ is thus equivalent to the parameter constraint $D = \mu H$.

It is apparent from Fig. 3 that the shapes of the curves corresponding to the FIA case are similar for both spin values assuming a maximum at $t = 0$ and monotonically decreasing with increase of temperature. By contrast, the shapes of the curves corresponding to the ZFS case differ depending on whether the spin is integer or half integer. For the integer spin ($S = 1$) the a vs. t curve is similar to that of the FIA case displaying consistently higher values, while for the half integer spin ($S = 3/2$) the corresponding curve displays a local maximum at the finite value of $t_{\max} \approx 0.37$ monotonically decreasing above $t_{\max}$. At the same time, for $S = 3/2$ the amplitude of a at $t = 0$ is lower in the ZFS case than in that of FIA.

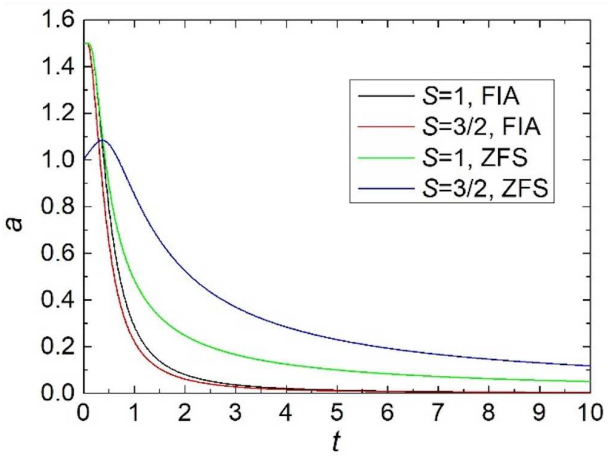

Fig. 3. Temperature dependence of the magnetic anisotropy parameter a given in Eq. (10) for the FIA (black or red), and ZFS (green or blue) case, and spin values of $S = 1$ (black or green) and $3/2$ (red or blue). Positive values indicate the easy-plane anisotropy. The plot presumes the parameter constraint $D = \mu H$.

Hence, at the lowest temperatures below the intersection temperature of $t_i \approx 0.30$ it is the field induced anisotropy that is more effective than the anisotropy due to the zero field splitting.

3. Conclusions

Two effects affecting the susceptibility tensor of a sample with non-interacting magnetic centers have been presented and compared, i.e., the anisotropy induced by the applied magnetic field and that due to the local interaction of the ZFS type. Integer and half integer spins were considered. The field induced anisotropy is of the easy-plane character and, under the parameter constraint of $g\mu_B SH = D$, it is inferior to that due to ZFS except for the case of the half integer spin at the lowest temperatures. At high temperatures the anisotropy parameter a collapses to zero in every case as expected. In most experimental cases the magnetic susceptibility is studied in low fields, e.g., 0.1 T or less, and the influence of FIA is negligible if ZFS is substantial. However, FIA rises in importance if one considers weakly anisotropic systems at low temperatures, especially those comprising half integer spins.

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