Low-energy spectrum of a Tm-based double-decker complex

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The magnetic and electronic properties of a Tm-based "double-decker" phtalocyanine complex are extensively investigated by several spectroscopic (optical absorption, inelastic neutron-scattering) and bulk (specific-heat) techniques. The resulting low-energy spectrum is exploited to obtain direct information on the ligand field. We show that the literature value of the second-order parameter A_2^0 is significantly overestimated and that the additional parameters arising from the true C_4 point symmetry (instead of the usually assumed ideal D_{4d} symmetry) at the rare-earth site cannot be neglected on this energy scale, while the presence of further symmetry reduction at low temperature is highly unlikely. The effect of the proposed ligand-field parameters on the relaxation properties of the Tb-based double-decker single-molecule magnet is briefly discussed.

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I. INTRODUCTION

Single-molecule magnets[1] (SMMs) are a particular class of magnetic molecules which exhibit magnetization hysteresis at low temperatures, i.e., whose physical properties resemble those of a macroscopic magnet. Typical examples of SMMs are transition-metal complexes such as Mn_{12} and Fe_8,[2] which have strong intramolecular exchange interactions (producing a high-spin ground state) and very weak magnetic interaction between molecules. It has been suggested that SMMs with better performances (higher anisotropy and blocking temperatures) might be produced if rare-earth or actinide elements are used. The first complex of this kind to be reported[3] was a lanthanide-based double-decker phtalocyanine (Pc) compound $[Pc_2R]^- \cdot TBA^+$ (TBA=tetra-*n*-butylammonium), in short Pc_2R (Fig. 1).[4] Evidence for slow magnetization relaxation in the complexes with $R=Tb^{3+}$ and Dy^{3+} was presented;[5] furthermore, Pc_2Tb was recently proposed as a building block for multidot devices in the emerging field of molecular spintronics.[6] Despite this, precise information on the ligand field and *f*-electron energy spectra (of crucial importance for studying and understanding the magnetic properties of these molecules) is still lacking.

The present work deals with experimental and theoretical results on the Pc_2Tm complex. This particular choice of rare earth was made because, although its double-decker complex does not qualify as a good molecular magnet because of its low ground-state spin, its low-energy spectra are supposed to be particularly rich; according to Ishikawa *et al.*,[7] five Tm^{3+} states should lie in the energy range between 0 and 3 meV. A combination of spectroscopic and low-temperature specific-heat measurements should then allow one to derive reliable values for all the ligand-field parameters and thus check the quality of previous estimates based on indirect measurements (e.g., magnetic susceptibility).

The paper is organized as follows. The ligand-field Hamiltonian which governs the magnetic properties of the rare-earth ions in this compound and the previously proposed ligand-field parameters and low-energy spectra (mainly determined on the basis of susceptibility measurements) are discussed. Then our direct determination of the position of the low-lying energy levels within the ground multiplet by optical absorption and neutron spectroscopy measurements is

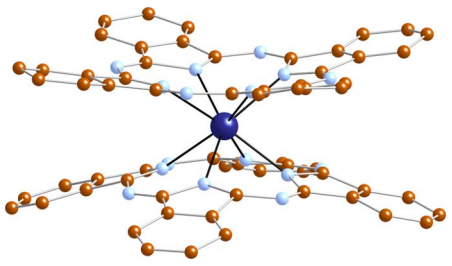

FIG. 1. (Color online) Structure of the Pc_2R complex. The large sphere at the center represents the trivalent rare-earth ion *R*. Light (cyan) and dark (orange) colored small spheres represent nitrogen and carbon atoms of the two Pc^{2-} rings, respectively. Hydrogens are not shown for clarity.

presented. The degeneracy of each energy level was determined by measuring and analyzing the specific heat of this complex. Three possible ligand-field schemes are proposed, but only one of them (which correctly reproduces both the field dependences of the specific heat and the magnetic-susceptibility measurements) is finally shown to be correct. A comparison between the so-obtained ligand-field parameters and those originally proposed for the series shows that the latter are only qualitatively correct, especially with regard to the effect of taking into account the ideal point symmetry instead of the true one.

II. LIGAND-FIELD PROPERTIES

In the approximate molecular symmetry D_{4d}, the ligand-field Hamiltonian acting on the Tm ion can be written as

$$H_{D_{4d}} = A_2^0\langle r^2\rangle \alpha O_2^0 + A_4^0\langle r^4\rangle \beta O_4^0 + A_6^0\langle r^6\rangle \gamma O_6^0, \qquad (1)$$

where the A_k^q's are the ligand-field parameters, $\langle r^k\rangle$'s are the expectation values of the r^k operator over the appropriate radial f-electron wave function, α, β, and γ are the Stevens multiplicative factors, and the O_k^q's are the Stevens operator equivalents.[8] Since only axial ligand-field terms appear in this Hamiltonian, the 13-fold degenerate $^3H_6$ ground multiplet of Tm^{3+} is split into six doublets $|\pm J_z\rangle$, $J_z=1,2,\ldots,6$, and one singlet with $J_z=0$ (choosing the z quantization direction along the C_4 symmetry axis). This ideal symmetry was chosen by Ishikawa *et al.*[7] to analyze their own magnetic susceptibility and NMR data for Pc_2R complexes with six different heavy rare earths.

However, if one wants to take into account the real C_4 symmetry established by x rays instead of the approximate D_{4d} one, two additional nonaxial ligand-field terms must be introduced,

$$H_{C_4} = H_{D_{4d}} + A_4^4\langle r^4\rangle \beta O_4^4 + A_6^4\langle r^6\rangle \gamma O_6^4. \qquad (2)$$

These operators have nonzero matrix elements only between states $|J_z\rangle$ and $|J_z'\rangle$ such that $|J_z - J_z'| = 4$; therefore, if nonaxial terms can be regarded as a perturbation with respect to $H_{D_{4d}}$ and all the energy levels of the latter are well separated, the only effect of the symmetry lowering from D_{4d} to C_4 is to split the $|\pm 2\rangle$ doublet.

III. RESULTS AND DISCUSSION

A. Experimental results

Optical spectroscopy measurements[9] have been performed by means of a Bomem DA8 Fourier transform spectrometer operating with an apodized resolution as fine as 0.025 meV. The sample was prepared under a stereomicroscope by assembling side by side (and partially overlapping) a few narrow and very thin (70–80 μm) polycrystalline needles of the compound. Sharp peaks attributable to electronic excitations of the Tm^{3+} ions have been clearly detected in the energy region corresponding to the $^3H_6 \rightarrow {}^3H_5$ transition (Fig. 2), the signal being weak due to the small sample thickness. The two intense structures which have been observed in this energy range are separated by about 2 meV and can be fitted by five Lorentzian-shaped peaks, centered at the same energies at 9 and 40 K (while the peak intensities and widths slightly change, as can be expected as a result of the different population of the low-energy states). Our preliminary ligand-field calculations showed that the two lowest levels of the excited $^3H_5$ multiplet are $|0\rangle$ and $|\pm 1\rangle$, the doublet being approximately 2.5 meV higher than the singlet. The two main peaks in the optical spectra could therefore stem either from transitions between the ground state and the two lowest-energy levels of the excited $^3H_5$ multiplet or from transitions to a single $^3H_5$ level from two groups of closely lying states of the $^3H_6$ multiplet separated by about 2 meV.[10]

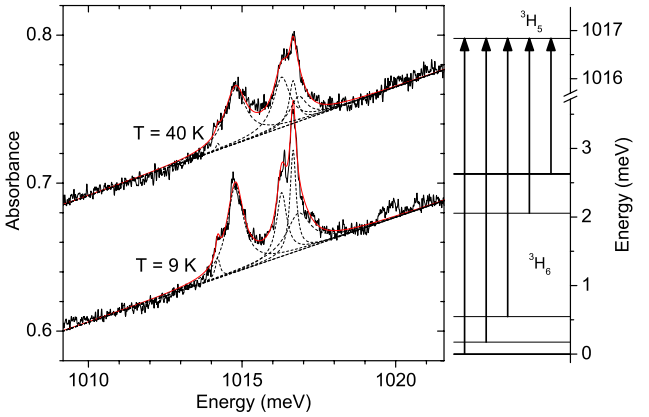

FIG. 2. (Color online) High-resolution optical-absorption spectra of Pc_2Tm at $T=9$ and 40 K. The signal between 1013 and 1018 meV can be fitted for both spectra with five Lorentzian-shaped peaks (shown separately as dashed lines) centered at temperature-independent values. The proposed level scheme and transitions are sketched on the right-hand side of the panel.

The latter hypothesis is shown to be correct as a 2 meV gap is directly observed by inelastic neutron scattering (INS).[11] Measurements were performed on the high energy transfer (HET) time-of-flight spectrometer at ISIS Spallation Source. Neutron scattering arising from a single magnetic center can be identified (and separated from other nonmagnetic contributions, for example, that of lattice vibrations) by its peculiar momentum-transfer ($\mathbf{Q}$) dependence, which is proportional to the square of the magnetic form factor of the relevant ion and therefore decreases with increasing Q. In our case, by comparing spectra at different values of Q, a clear magnetic signal around 2 meV was revealed, superimposed to the elastic peak tail and arising from the superposition of two dipole-allowed intramultiplet transitions (Fig. 3). The capabilities of this large-energy-transfer instrument were fully exploited to search for other intramultiplet magnetic transitions up to 90 meV, but none were detected.

The combined optical and neutron spectroscopies allow us to conclude that four excited energy levels are lying just above the ground state and precisely at 0.18, 0.55, 2.09, and 2.64 meV (see level schemes on the right-hand side of Figs. 2 and 3); these values stem from the experimental separations of the four lower energy Lorentzian peaks from the highest energy one peaking at about 1017 meV in the optical spectra (Fig. 2). The very weak peak observed in the optical-

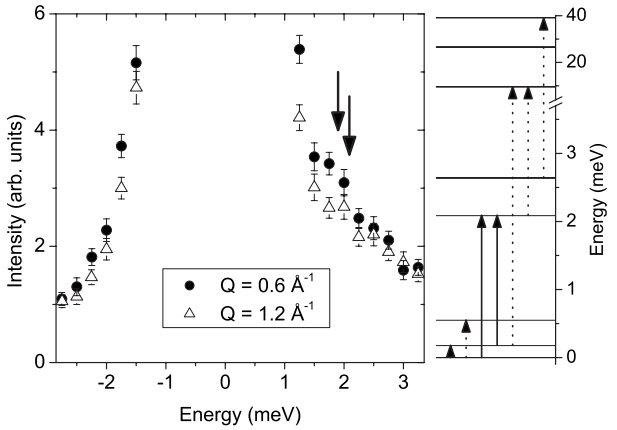

FIG. 3. Inelastic neutron-scattering spectra of Pc_2Tm at $T=4$ K and incident energy $E_i=18$ meV. Full dots indicate spectra from the low-angle bank; open triangles those from the high-angle one. The corresponding value of the momentum transfer Q (for energy transfer $\hbar\omega=2$ meV) is given in the legend. The proposed level scheme and dipole-allowed transitions are sketched on the right-hand side of the panel. The position of the two transitions marked by continuous arrows on the sketch is indicated by black arrows on the INS spectra. Transitions indicated by broken lines were too weak to be observed in this experiment.

absorption spectra at about 1020 meV can be attributed to a transition between the ground state of the $^3H_6$ multiplet and the second aforementioned doublet level of the excited $^3H_5$ multiplet.

In order to get information on the degeneracy of these low-energy ground-multiplet sublevels, specific-heat measurements as a function of temperature and magnetic field (Fig. 4) have been performed on a 14 T Quantum Design physical properties measurements system (PPMS-14T),

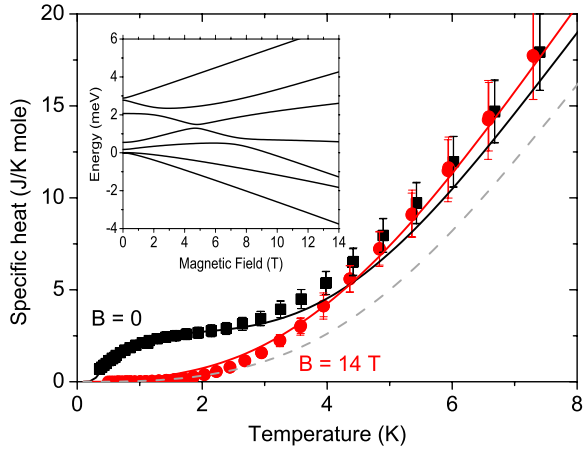

FIG. 4. (Color online) Symbols: temperature dependence of the specific heat of Pc_2Tm, with (dots) and without (squares) a 14 T applied magnetic field. Continuous lines: calculations based on the ligand-field parameters of model A (see main text for details). The same calculations performed using the parameters of models B and C give almost undistinguishable results and are therefore not shown. Dashed line: Debye lattice contribution ($T_D=50$ K). Inset: low-energy spectra calculated with a magnetic field applied along the direction given by the polar and azimuthal angles $\theta=\phi=\pi/4$.

TABLE I. Ligand-field parameters for models A, B, and C (see main text for details). The value of A_6^4 was arbitrarily fixed to zero. Only model A allows one to reproduce all available experimental data.

Parameter (meV)	Model A	Model B	Model C
$A_2^0\langle r^2\rangle$	15.8	11.8	33.4
$A_4^0\langle r^4\rangle$	−16.0	−11.7	−35.0
$A_6^0\langle r^6\rangle$	4.84	3.29	11.7
$A_4^4\langle r^4\rangle$	±7.33	±1.36	±5.88
$A_6^4\langle r^6\rangle$	0	0	0

which can achieve temperatures down to 330 mK using the ^{3}He insert. The curve taken at 14 T clearly shows that the lattice contribution is very close to zero at least up to 2 K; attempts to reproduce this low-temperature part of the zero-field curve show that the ground state must necessarily be a doublet, and the lowest-lying excited states at 0.18 and 0.55 meV must be singlets (any other attempts would largely overestimate the specific-heat value between 0.5 and 2 K).

B. Ligand-field analysis

From Sec. II we know that singlet levels in C_4 symmetry are most likely either $|0\rangle$ or a combination of the $|\pm2\rangle$ states. Incidentally, we note that the fact that at least two singlets appear means that the spectra cannot be reproduced with the D_{4d} axial parameters only. However, the observed singlets are relatively close in energy, so the additional C_4 terms can probably be regarded as a perturbation. Nevertheless, we have performed our calculations by diagonalizing the full C_4 ligand-field Hamiltonian (2). A thorough search in the parameter space was made possible by the fact that, if only the ground J multiplet is considered, Hamiltonian (2) can be diagonalized analytically.

We looked for possible sets of ligand-field parameters which respect the three following constraints: (i) the energy positions and the multiplicities of the lowest-lying levels must reproduce the experimental results in Sec. III A; (ii) the ground and the first-excited states should have low spin in order to reproduce the low-temperature magnetic susceptibility; and (iii) since, at first order, the only effect of A_4^4 and A_6^4 is to split the $|\pm2\rangle$ doublet, A_6^4 was fixed at zero value to avoid overparametrization. Within these assumptions, only three possible sets of parameters (given in Table I as models A–C) have been found; in all cases, the $|\pm1\rangle$ doublet is the lowest-energy level, followed by three singlets and by the $|\pm6\rangle$ doublet, the latter located 2.64 meV above the ground state.[12] From the point of view of the low-energy spectra, then, the only difference between the three models is the position of the $|0\rangle$ singlet and of the D_{4d} $|\pm2\rangle$ doublet before the latter is split by A_4^4 (Fig. 5). It can be noticed that the parameters in the different sets are quite different, although the three models agree on their signs and order of magnitude; also the D_{4d} axial parameters proposed by Ishikawa *et al.*[7] are in qualitative agreement from this point of view.

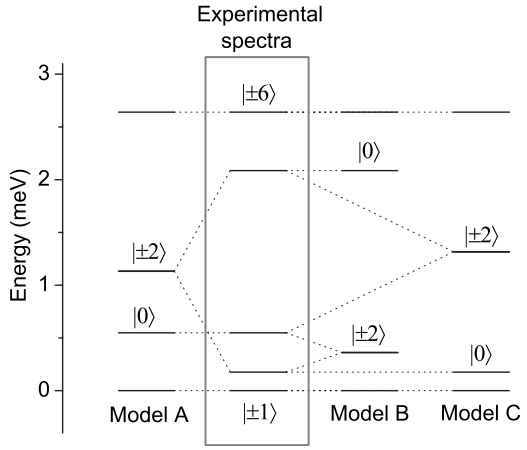

FIG. 5. Energy levels and wave functions relative to the axial ligand-field parameters (D_{4d}) of models A–C. With the addition of the nonaxial A_4^4 parameter (C_4), which splits the $|\pm 2\rangle$ doublet, all the three models correctly reproduce the experimental optical and neutron spectra.

While all the models display at least one magnetic-dipole-allowed transition at about 2 meV (necessary to understand the neutron results in Fig. 3) and correctly reproduce the low-temperature specific-heat curves at 0 and 14 T (Fig. 4), significant differences arise when we compare the calculations for other observables. The magnetic-field dependence of the specific heat, for example, displays a characteristic peak whose maximum shifts toward higher field values when the temperature is increased (Fig. 6). This behavior is well reproduced by models A and C, while the curves calculated with model B display a double-peak structure. As for the magnetic susceptibility, the measured values given in Ref. 7 are well reproduced by models A and B, while model C overestimates the experimental curve at low temperatures (Fig. 7). We therefore conclude that only calculations based on model A are in agreement with all available experimental data.

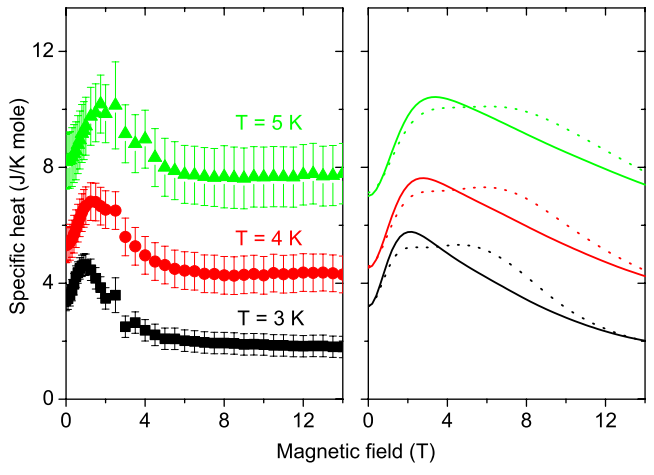

FIG. 6. (Color online) Left panel: measured magnetic-field dependence of the specific heat of Pc_2Tm at $T=3$, 4, and 5 K. Right panel: calculations based on the ligand-field parameters of model A (continuous lines) and model B (dashed lines). Model C yields results similar to model A for this observable; therefore the corresponding calculations are not shown in the figure.

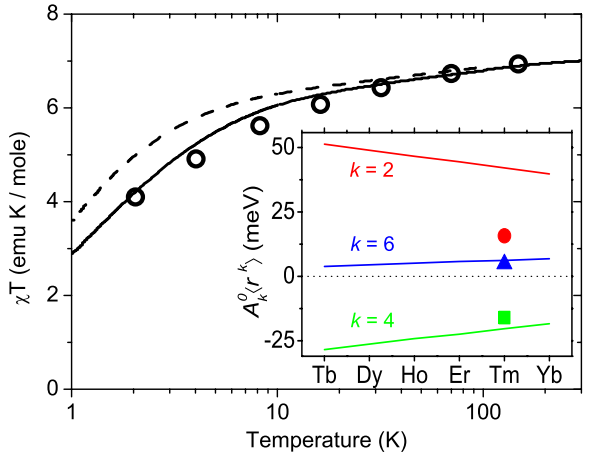

FIG. 7. (Color online) Magnetic susceptibility of Pc_2Tm. Dots: experimental data (from Ref. 7). Full line: calculations with ligand-field parameters from model A. Dashed line: calculations with ligand-field parameters from model C. Inset: axial ligand-field parameters A_k^0 for $[Pc_2R]^-\cdot TBA^+$. Lines: values for the heavy rare earths proposed in Ref. 7. Symbols: values for R=Tm obtained in the present work (model A).

IV. CONCLUSIONS

The C_4 ligand-field parameters for the $[Pc_2Tm]^-\cdot TBA^+$ complex have been determined by performing several experimental measurements and analyzing the results. Our values of the parameters are compared with those previously proposed[7] in the inset of Fig. 7. One can see that, while A_4^0 and A_6^0 are perfectly in line with the values given in Ref. 7, A_2^0 was largely overestimated.

Keeping into account that the A_k^q parameters are not expected to change significantly when considering different rare earths embedded in the same compound,[8] this could have led to wrong estimates of the anisotropy barrier of Pc_2R single-molecule magnets (R=Tb and Dy). Let us consider the Tb-based complex as an example. Ishikawa *et al.*[5] studied the slow relaxation of the magnetization in Pc_2Tb and found that Orbach processes are dominant in the high-temperature range, with an effective barrier height U_{eff} of about 32 meV (experimental value). Since Orbach processes require as the first step the direct absorption of a phonon by the spin system (in order to excite it to higher energy states), the value of U_{eff} should be larger than (or equal to) the energy gap Δ_0 between the ground and the first-excited energy levels. By using the ligand-field parameters given in Ref. 7 one can calculate $\Delta_0 \simeq 55$ meV. This might be an indication that the literature value of A_2^0 (and, as a consequence, that of Δ_0) is actually overestimated. As a test, we have calculated the energy spectra of the Pc_2Tb complex using the A_k^q parameters determined in this work for Pc_2Tm and the radial averages found in Ref. 13; the value of Δ_0 is reduced to about 27 meV, which appears to be more in line with the available experimental relaxation data.

In principle, Δ_0 could be measured experimentally for the Pc_2Tb complex by INS; however, a large quantity of deuterated sample would be necessary since the relevant transition would appear in an energy range where phononic scattering usually prevails. Unfortunately, in this case the (already available) susceptibility measurements are of little help because the separation in energy between the ground state and the rest of the multiplet is so large that this observable is only influenced by the $|\pm 6\rangle$ doublet. Mössbauer measurements on the Gd-based analog, on the other hand, could be used to determine the electric field gradient at the rare-earth site, which is directly proportional to A_2^0. Overall, a systematic study of the ligand-field parameters of Pc_2R, determined by a combination of several techniques, along the whole series of rare earths would perhaps be the best way to check the above statement.

The effect of the ligand-field parameters (such as A_4^4) which are forbidden in the ideal D_{4d} but allowed in the true C_4 point symmetry of the rare-earth ion was clearly detected in the low-energy spectra of Pc_2Tm. Further symmetry lowering should add to Hamiltonian (2), among others, a term proportional to O_2^2; this would split the ground $|\pm 1\rangle$ doublet and would therefore be detectable, for example, by specific-heat measurements at very low temperatures. Given that no such effects have been observed in the temperature range that we have investigated, we can conclude that, if present at all, such a term has an upper bound $|A_2^2\langle r^2\rangle| \ll 0.05$ meV and is therefore negligible for most purposes.

ACKNOWLEDGMENT

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