Racah algebra and x-ray *sum rules* in magnetism of solids

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Abstract

This is an overview of the role played by G. Racah's "Theory of Complex Spectra" in new experiments based on x-ray spectroscopy, and mainly on magnetism of solids. The "Theory of Simple Spectra" by B. T. Thole, G. van der Laan and P. Carra is presented and some of the fields of interest reviewed.

1 Introduction

1.1 The Theory of Complex Spectra

In a remarkable series of Physical Review papers [2, 3, 4, 5] Giulio Racah established in less than a decade the group-theoretical basis allowing the correct interpretation of spectroscopy experiments on non-trivial atomic, nuclear and elementary particle physics.

Previously to Racah's pioneering work, only simple and rather particular cases, involving a small number of angular momenta could be correctly tackled, involving lengthy calculations of Slater integrals even in the most favourable cases. The standard book was E. U. Condon and G.H. Shortley's "The Theory of Atomic Spectra" [1]. In practice, the calculations were usually unaffordable. G. Racah developed a spherical tensor technique, the so called *Wigner-Racah algebra*, allowing to calculate the energies of electronic configurations in a growing scale of difficulty: first two electrons and rather simple three-electron configurations [2], then the more complex situations for $l = 1$ and 2 (describing the electronic shells of transition metals of the d series) [3, 4], and finally, the f^n configurations [5] which from an electronic-shell point of view correspond to lanthanides and actinides. Thus, the four-paper series provides the full artillery needed to interpret atomic spectroscopy experiments along the whole periodic table of the elements, and to understand in detail the origin of the main ingredient of solid-state magnetism: electronic angular momenta.

1.2 Crystal field and magnetism

Magnetism of solids is no more (but no less) than addition of electronic angular momenta and the (usually complex) interactions between them. The role of Racah algebra in our understanding of magnetism is therefore a very important one, and its impact spans on several areas. It has been traditionally linked to the theory of crystal field interaction. The combination of Hans Bethe's crystal field theory [6] and Giulio Racah's algebra allowed Y. Tanabe and S. Sugano [7, 8, 9] to properly describe the energies and electronic states of d transition ions within solids (strong and intermediate crystal fields). The solution depends on the symmetry of the site occupied by the ion. It is easy to show that in most cases, the mixing of the free-ion electronic states by the crystal field interaction has a very small (or zero) expectation value for the orbital magnetic moment in a given axis of quantisation. This is the so-called "quenching" of the orbital momentum by crystal electric field, which leads to the spin-only magnetic moments of $3d$ magnets, in very good agreement with experiment [10]. Only the spin-orbit interaction, weaker than the crystal field in d ions injects some unbalance in the otherwise symmetric $\langle L_z \rangle = 0$ situation. This fact is of the highest interest in magnetism and its applications, as the orbital magnetic moment is the microscopic origin of the magnetic anisotropy energy and therefore, of any useful magnet. However, the separate determination of orbital magnetic moments has been an elusive objective of the classical magnetometries.

The crystal field theory had an remarkable success explaining the puzzling spectra obtained from *rare-earth* ($4f$) ions. The solution was supplied in a simultaneous and independent manner by B. R. Judd [11] and G. S. Ofelt [12]. Lanthanides are very different to $3d$ ions: the $4f$ unfilled shell is strongly screened by the occupied $5s^2 5p^6 6s^2$ shells, and the crystal field interaction has to be treated as a perturbation of the spin-orbit interaction. The Hund rules determine the L, S, and J values of the ground state term, which is splitted in mixed $|J_z\rangle$ states by crystal fields. The details of the spectra are very complicated, and the magnetic properties of the ground state usually hard to predict, although the bases of the theory are fully developed [13]. The usually large orbital momenta in rare earths are at the origin of its huge magnetic anisotropy. Indeed, the *metallurgical recipe* [14] of high-quality modern magnets stands on the (ferromagnetic) addition of the cheap magnetic moment of Fe or Co, to the extremely anisotropic moment of Nd or Sm. The development of low-prize, small-volume, high-power rare-earth – iron magnets has contributed significatively to change our everyday technology in the last two decades.

1.3 Some technical achievements

The application of Racah algebra methods to interpret interesting spectra in chemistry and solid state physics required the evaluation of matrix elements of Coulomb or multipole interaction operators between atomic or molecular states in non-trivial cases. Three main steps were needed to fulfill this objective: the developement of graphical methods (the Yutsis graphs) for representing the recoupling coefficients and reduction rules leading to summation formulae [15], Judd's reformulation of Racah's work on a second quantization basis [16] and the implemen-

tation of computer codes allowing to timely calculate spectra in different energy ranges and experiments. In particular, the Hartree-Fock based atomic structure code by Robert D. Cowan has had a great impact on solid-state and molecular spectroscopy [17, 18]. The extension of the Hartree-Fock calculations with hybridization and point group symmetry, as is mandatory in molecules and solids, allowed to calculate the transitions from the ground state to every allowed final state.

The success of the implementation of the *Theory of Complex Spectra* to solids and molecules (now usually referred to as "*multiplet theory*") is remarkable: in principle it is possible to analyze not only x-ray absorption spectra, but also photoemission, resonant x-ray scattering, as well as polarisation dependent experiments. Such a calculation should allow to understand the local electronic structure (and therefore the chemical bonding) of molecules and solids. However, usually there are too many relevant unknowns which complicate the fulfillment of such an ambitious program: the relative strength of spin-orbit interaction and exchange, the details of crystal field (in particular the role played by conduction electrons), among others which seriously difficult our ability to determine the final states, specially in solids. Properly performing "multiplet calculations" is complicated, and in practice almost exclusively specialized theorists are succesfully devoted to them (even if a "*Hitchhiker's guide*" to the subject is available [19]).

2   Theory of Simple Spectra

With the advent of condensed-matter dedicated synchrotrons *circa* 1980, x-ray absorption and emission become routine techniques. In those years, the volume of scientific production in molecular chemistry, condensed matter physics and materials science was too large to undertake the effort of studying the details of each spectra. Only some special cases deserved to be studied with such degree of refinement. Moreover, after 1990, several facts opened the possibility to study not only the spectra but its variations with other parameters. In particular, the possibility to choose the polarisation of synchrotron radiation (circular or linear in any direction) thanks to new sources known as "insertion devices" and a greatly improved quality of the experimental spectra (due to advances in brilliance, stability of the beam and detector sensitivities), allowed to study the dependence of absorption with the polarisation of the incoming beam. These *dichroic* spectra, among which the X-ray Magnetic Circular Dichroism (XMCD) has become the paradigmatic example [20, 21, 22], are harder to fit with the whole Racah-algebra machinery than absorption itself: small variations in the spin-orbit or exchange energies of initial or final states provoke dramatic differences in dichroic spectra, as XMCD intensities are very often not larger than 1%.

After the advent of third-generation synchrotron radiation sources in the 1990's, XMCD become an almost-routine technique, although pioneer works were performed earlier in Munich [23] and Groningen [24]. In 1984, Theo Thole joined George Sawatzky's group at the University of Groningen as a postdoc. This group was measuring X-ray spectroscopy of transition metals in solids and molecules at the *Anneau de collision* (ACO) in Orsay, and Thole's subject was to

write a code allowing to simulate the experimental spectra. Although the initial suggestion was to start from scratch, finally it was decided to adapt Cowan's codes by extending the Hartree-Fock calculations with hybridization and point group symmetry, as is mandatory in molecules and solids. Theo's code for hybridization was written in collaboration with Akio Kotani, one of the founding fathers of the present japanese spectroscopy school. By the way, the original routine which applied Wigner-Eckart theorem to obtain reduced matrix elements in any point group, which had been developed by P.H. Butler [25], was called "RACAH" by Thole. While Thole was working on the theoretical spectroscopy program, he coincided in Groningen with G. van der Laan, a former fellow student. Together, they envisaged a research program aiming to provide experimenters with simpler analysis tools. Thole and van der Laan coined this program "*Theory of Simple Spectra*" [26] in clear reference to Racah's original Physical Review papers. These tools took the form of *sum rules*, relating the integrals of the spectra to the expected values of different quantum operators in the ground state.

2.1 The spin-orbit sum rule

Theo Thole and Gerrit van der Laan [27, 28] first developed a sum rule relating the integral of the unpolarized x-ray absorption spectrum over the spin-orbit split $j = l \pm 1/2$ core edges to the expectation value of the ground-state spin-orbit operator. A systematic study of the *branching ratio* in X-ray absorption (the ratio between the absorption observed at the L_3 ($2p_{3/2}$) and L_2 edges ($2p_{1/2}$) evidenced strong deviations from the statistical value for the spin-orbit split p to d absorption in transition metals and d to f absorption in rare-earth metals, which were not understood at that time. By means of graphical methods which were carefully checked by numerical computation, Thole showed that the branching ratio was directly proportional to the spin-orbit coupling in the ground state: only if L and S are good quantum numbers, the branching ratio is purely statistical (2:1 in $L_{3,2}$ edges). Any deviation from the statistical value indicates spin-orbit splitting in the initial (i.e. ground) state.

The expectation value of the spin-orbit operator $\mathcal{Z} = \sum_i \mathbf{l}_i \mathbf{s}_i$ can be determined by a simple measurement of the branching ratio, thanks to the linear relationship (which is exact for dipole transitions $l^n \to cl^{n+1}$) [28]:

$$B_j(\Psi) = \frac{2j+1}{2(2c+1)} \pm A(c,l,n)\langle\Psi|\mathcal{Z}|\Psi\rangle \qquad (1)$$

where the $\pm$ sign is for the two $j = c \pm 1/2$ edges, respectively. The proportionality constant $A(c,l,n)$ depends on the total angular momentum of the core hole c, the l of the valence electron and on the number of electrons n, and was tabulated on the original manuscript [28]. In Fig. 1 the $L_{2,3}$ x-ray absorption of a sample of Pt_{13} clusters dispersed in the cages of a Na-Y zeolite structure [29] is shown. Besides its potential interest in fuel catalysis, this experiment exemplifies how easy is to put in evidence a non zero $\langle\mathcal{Z}\rangle$ value. However, although related with the magnetic moment of a system, the sum rule on the expected value of the spin-orbit operator has for some time lay dormant. However, it has recently made a comeback in the research on actinides, where the spin-orbit interaction is very strong [30]. Nevertheless, the use of this first sum-rule

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has been relatively scarce: the impact of Refs. [27] and [28] has been stabilized with less than a *hundred* citations, while the magnetic sum rules to be presented later have received more than one *thousand* each since 1992, and counting.
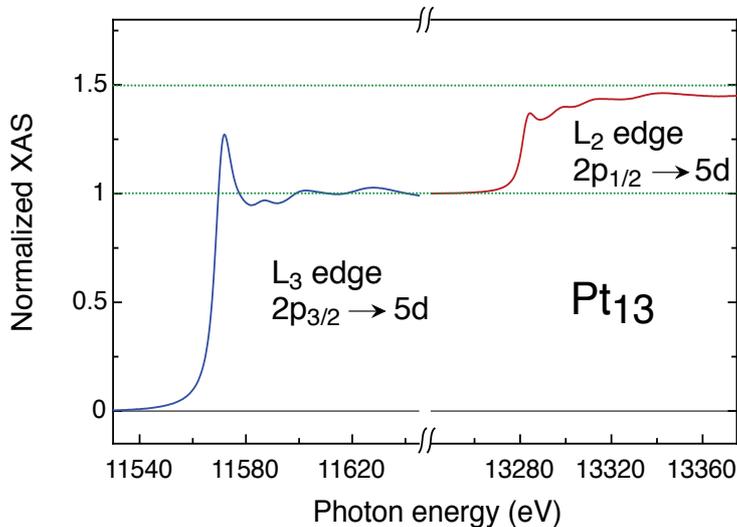
Figura 1.— X-ray absorption at the Pt $L_{2,3}$ edges recorded on a sample of Pt_{13} clusters. The departure of the statistical 2:1 branching ratio is exemplified after normalizing the signals to 1 at the L_3 edge: the XAS signal well above the edge is clearly below 1.5, indicating a non zero $\langle \mathcal{Z} \rangle$ value.

2.2 The XMCD sum rules

XMCD is the difference of absorption $\Delta\mu = \mu^{-1} - \mu^{+1}$ of left (-1) and right (+1) circularly polarized light due to the dependence of the selection rules with the relative orientation of the photon helicity and the angular momentum of the absorbing atom. Experimentally, this relative orientation can be chosen by an applied magnetic field or by changing the polarisation.

It is relatively easy to show [31] that, in selected cases, the XMCD signal is proportional to the magnetization of the absorbing sublattice. As the edge energies are characteristics of each element, XMCD is an element-specific, extremely powerful magnetometry. XMCD is obviously related with the *optical activity* induced in matter by a longitudinal magnetic field as first shown by Faraday in the visible range.

2.2.1 THE ORBITAL SUM RULE

Systematic trends of the integrated dichroic signal, and a dependence of integrated intensity on the spin-orbit splitting became evident. Again by using diagrammatic techniques Thole was able to derive [32] the following relationship between the expected value of the third component

of the orbital moment in the ground state;

$$\langle L_z \rangle = \frac{2l(l+1)(4l+2-n)}{l(l+1)+2-c(c+1)} \times \frac{\int_{j_++j_-} d\omega(\mu^{-1}-\mu^1)}{\int_{j_++j_-} d\omega(\mu^{-1}+\mu^1+\mu^0)} \tag{2}$$

in units of $\hbar$, where the total angular momentum of the core hole and the valence electron are respectively c and l and n is the number of electrons in the valence shell (therefore, $(4l+2-n)$ is the number of holes available in the absorbing shell in the ground state). The integral $\int_{j_++j_-} d\omega(\mu^{-1}+\mu^1+\mu^0)$ is 3 times the averaged absorption for unpolarized light, and is introduced into the equations for normalization. Note that (2) is independent of the radial integrals.

2.2.2 THE SPIN SUM RULE

M. Altarelli found a simpler proof of the orbital sum rule (2), based on one-electron Slater determinants [33]. This finding paved the way to the derivation, by Carra and Thole, of the second sum rule for magnetic dichroism [34], which related the spin moment and the magnetic dipole term to the weighted difference of the spin-orbit split dichroic signal:

$$\frac{\int_{j_+} d\omega(\mu^{-1}-\mu^1) - [(c+1)/c]\int_{j_-} d\omega(\mu^{-1}-\mu^1)}{\int_{j_++j_-} d\omega(\mu^{-1}+\mu^1+\mu^0)} \times (4l+2-n) =$$

$$\frac{c(c+1)+2-l(l+1)}{3c}\langle S_z \rangle - \frac{l(l+1)\left[l(l+1)+2c(c+1)+4\right]-3(c-1)^2(c+2^2)}{6lc(l+1)}\langle T_z \rangle \tag{3}$$

where $\langle T_z \rangle$ is the magnetic dipole operator, whose expectation value provides a measure of the anisotropy of the field of the spins when the atomic cloud is distorted, either by the spin-orbit interaction or by crystal-field effects [35]. The expected value of the spin moment can be accurately obtained for those cases in which $\langle T_z \rangle$ can be determined: $\langle T_z \rangle$ is small in cubic 3d systems, it can be analytically calculated in $M_{4,5}$ edges of rare earths and actinides, and it is zero in $l=0$ configurations. In other cases, $\langle T_z \rangle$ can be extracted from angular-dependent measurements. Otherwise, only the value for an "effective spin" operator, mixing $\langle S_z \rangle$ and $\langle T_z \rangle$ can be experimentally determined.

The theory department of the European Synchrotron Radiation Facility (ESRF), directed first by Massimo Altarelli and later by Paolo Carra, grouped the efforts of a small but very active team of scientists that Theo Thole joined for long stays during the first years of the nineties. Their work, in close contact to the development of several x-ray techniques at the ESRF beamlines [36, 37, 38, 39, 40] has had a worldwide impact in the development of x-ray scattering techniques and the design of new sources.

Unfortunately, Theo Thole (1950-1996) and Paolo Carra (1952-2005) passed away by far too soon. Of the pioneering group, only Gerrit van der Laan worked further on the development of the *Theory of Simple Spectra*, looking forward and beyond XMCD sum rules to higher statistical momenta, to extract the maximum information from experimental x-ray spectra [41].

3 The short and winding way to the bottom

In his famous talk *"There's plenty of room at the bottom"* [42], Richard Feynman foresaw the advent of a nanotechnological future, which today is a reality in condensed matter research and also partly in consumer electronics. Third generation synchrotron sources are very well suited to study nanoscopic systems due to its extreme brilliance: the x-ray spots are microscopic while maintaining an extremely high photon flux. This allows the study of extremely small samples. For example, the amount of Pt probed in the experiment of Fig. 1 is tiny, and the possibility to study in detail its magnetism, as shown in Fig. 2 and Ref. [29] is somehow astonishing. Indeed, one of the most reassuring properties of XMCD is its element selectivity, which ensures that the observed magnetization in Fig. 2 has its origin in nothing but Pt, ruling out any spurious source of magnetism, in contrast with other highly sensitive magnetometries [43, 44, 45].
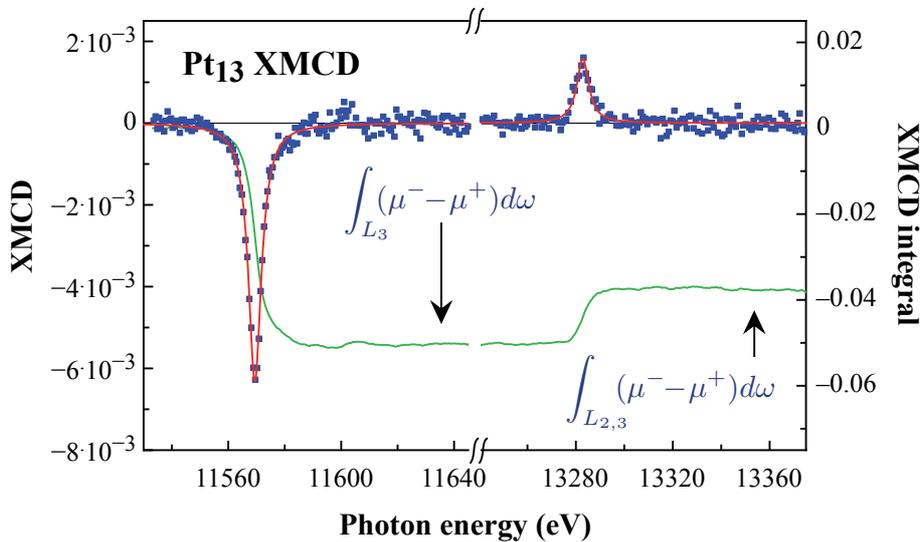
Figura 2.— X-ray Magnetic Circular Dichroism at the Pt $L_{2,3}$ edges recorded on a Pt_{13} cluster, in the same units of Fig. 1. The observed XMCD signal is clearly larger than expected for usual Pauli paramagnetism in bulk Pt. This demonstrates the establishment of a magnetic moment on Pt_{13} clusters due to a finite-size effect on the Pt electronic structure.

As clearly shown in Fig. 3 the integrals involved in the magnetooptical sum rules (equations 2 and 3) are relatively simple to obtain, except in the case of extremely small magnetic moments ($\mu \leq 10^{-3}\mu_B$).

4 Orbital moments and magnetic anisotropy

Among many examples in the recent literature, sum rules have been recently applied to study the magnetic moments of molecules as Fe-phtalocyanine (FePc). Appart of its large industrial uses, metal phthalocyanines are simple model molecules for the understanding of the electronic properties of metals in complexes. In spite of extensive work on them, their magnetic properties

are not fully understood. In FePc, the Fe atom has square-planar coordination with four pyrrolic N atoms (see Fig. 3, left). In the bulk and thin films these planar molecules form linear chains by columnar stacking. The molecule fourfold axis is tilted with respect to the crystal b axis by an angle ϕ. In the bulk form two phases appear; the α-FePc with a tilting angle of $\phi = 26.5°$, and the β-phase with $\phi = 44.8°$. The former becomes ferromagnetic below $T_C \sim 10$ K in the bulk form while the latter is paramagnetic down to liquid helium temperatures.
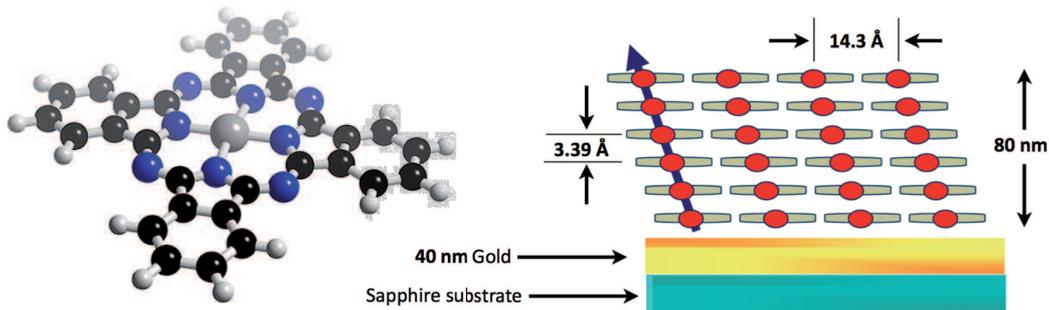
Figura 3.— Left: Artist view of an FePc molecule. The Fe is the central atom (gray) bonded to the 4 pyrrolic N (blue). Other four N atoms (blue) bridge the organic structures formed by the C (black) and H (white) atoms. The molecule is plane to a very good approximation. Right: Schematic view of the columnar film FePc sample indicating its dimensions.

Thin films of FePc are deposited on a smooth gold substrate with the molecule plane lying flat on the substrate plane. The thin film sample in this work was prepared in an organic molecular beam epitaxy (OMBE) system at the Physics Department of the UCSD. In thin films grown by OMBE the molecule plane orientation is set by a proper substrate selection and the growth conditions. In order to obtain α-phase FePc films with the molecule plane parallel to the sapphire substrate, first a 40 nm nominal thickness Au buffer layer was deposited. Without breaking vacuum, the FePc was deposited from a crucible set to 350 °C, while the substrate was maintained at 150 °C to increase the crystallite size. The typical growth rate was 0.9 Å/s. The FePc deposition rate is determined by means of a quartz crystal monitor before and after the deposition. The FePc thickness of the investigated sample was 80 nm.

We have measured a sample of such columnar thin films as shown in Fig. 4 (right). The orientation of a column parallel to the substrate can not be controlled, and therefore any anisotropy within the plane is averaged out in the experiment. The relevant x-ray spectra obtained in normal incidence are shown in Fig. 4. Panel a shows the x-ray absorption spectra in the vicinities of the Fe L$_{2,3}$ edges recorded with left- (blue) and right-polarised light (red), together with the integral of the averaged, unpolarised absorption, the normalization value appearing in eqns. 2 and 3. The XMCD signal (green) is shown in the panel b of Fig. 4. In Fig. 4(c) the values of the
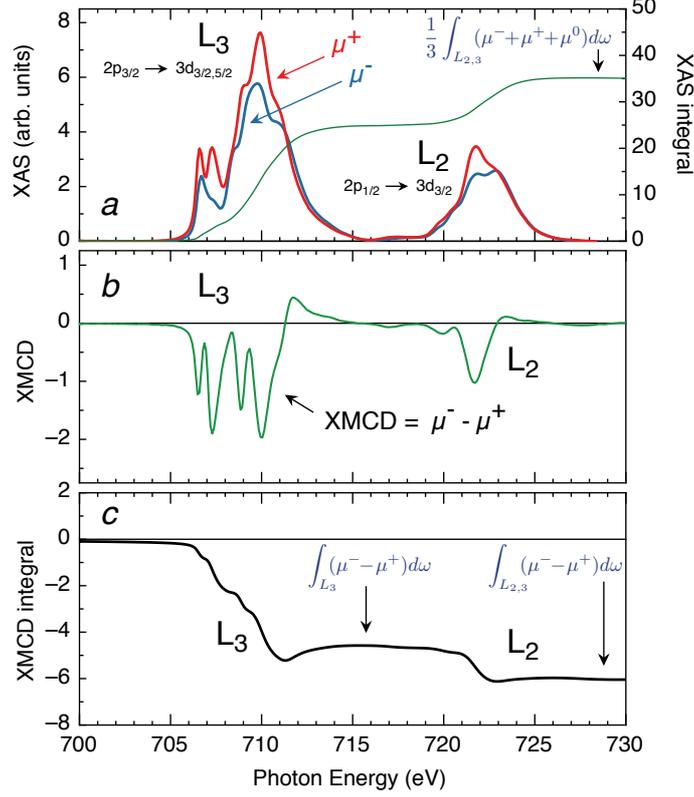
Figura 4.— *a)* X-ray absorption spectra with right (red) and left (blue) circularly polarised light at the Fe $L_{2,3}$ edges on the FePc thin film sample. The integral of the averaged unpolarised absorption is also shown (green). *b)* X-ray Magnetic Circular Dichroism obtained from the XAS spectra shown in the upper pannel. *c)* Integral of the XMCD signal. Panels *a)* and *c)* identify the relevant integrals in the sum rules (2) and (3) with the experimental values.

integrated XMCD with upper integration limits at the respective arrows, have been depicted. Similar spectra and analysis are performed at different incidence angles, from normal to grazing incidence. The detailed analysis has been published [46] and the results are shown in Table 1.

The orbital moment is anisotropic, being largest when the applied field is parallel to the xy molecule plane, which is in agreement with magnetization results [46]. Its value is $m_L^{xy} = 0.53 \pm 0.04 \mu_\text{B}$. In spite of the applied approximations, and the inherent experimental uncertainty, the existence of an extraordinarily large, highly unquenched orbital moment in FePc is proven beyond doubt.

With the experimentally determined values of m_L^{xy}, m_L^z, and m_T^z it is possible to derive an estimation of the Magnetocrystalline Anisotropy Energy originating from spin-orbit coupling by means of the Bruno-van der Laan model [47, 48]:

$$\Delta E_{SO} = -\frac{G}{H}\left(\frac{\xi_{3d}(m_L^z - m_L^{xy})}{4\mu_\text{B}} + \frac{\xi_{3d}^2((\frac{21}{2})(\frac{3}{2})m_T^z + A)}{\Delta E_{ex}\mu_\text{B}}\right) \qquad (4)$$

where G/H $\approx$ 0.2 for transition metals, $\xi = 0.05$ eV for Fe, and $\Delta E_{ex} = 1$ eV is the energy

Table 1.— The magnetic moment (orbital, spin and dipolar, in units of μ_B) obtained from the XMCD sum rule results, and the calculated orbital to spin moment ratio.

m_L^{xy}	m_L^z	m_S	m_T^z	m_T^{xy}	m_L^{xy}/m_S
0.53(4)	0.29(5)	0.64(5)	0.074(5)	-0.037(5)	0.83(4)

shift between the majority and minority states. The first term corresponds to the anisotropy originating from the difference in orbital moment between the perpendicular and parallel directions to the substrate plate (thus of orbital origin), and the second term from the intra-atomic dipolar term, describing the anisotropy in the spin density. Replacing the numerical values, one gets $\Delta E_{SO} \approx +6.0 \times 10^{-4} - 5.3 \times 10^{-4} = 7 \times 10^{-5}$ eV. Thus, the orbital term and the dipolar term are of the same order of magnitude and are competing with each other. The sign is positive, thus favoring xy anisotropy. Since the anisotropy field was estimated as $\mu_0 H_A = 0.6$ T, the anisotropy (volume) constant can be evaluated as $|K_1| = \mu_0 H_A M_s/2$, yielding $K_1 = -2.2 \times 10^3$ J/m^3, or $\Delta E_{SO} = 2.1 \times 10^{-5}$ eV/atom, assuming the specific volume of Fe atoms as $v = 1.48 \times 10^{-28}$ m^3, as in α-FePc. The experimental value is of the same order of magnitude as the theoretical estimation from Eq. 4, although somewhat lower. Of course, Eq. 4 is just a rough approximation since the original model is derived for a fully occupied majority band, and a completely empty minority band, which is not our case, but it justifies qualitatively our finding of xy anisotropy in FePc.

5 Conclusions

The impact of Giulio Racah's work on magnetism cannot be overvalued and indeed, it is well known since decades. The recent development of third-generation synchrotron radiation sources have allowed the establishment of element-specific magnetometries based on X-ray absorption and scattering. The proper use of Racah-Wigner algebra in molecules and solids not only allows the detailed understanding of the experimental spectra, but also led to the formulation, by Theo Thole and coworkers, of simple *sum rules* allowing the separate determination of orbital and spin magnetic moments. These late products of Racah's methods have had a great impact on today magnetism, as scientific literature continuously corroborates.

Acknowledgements

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