

SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

19 April - 21 May 2004

Miramare - Trieste, Italy

1561/24

Introduction to X-Ray Magnetic Scattering

Massimo Altarelli

X-ray Magnetic Scattering : Theoretical Introduction

Massimo Altarelli

Sincrotrone Trieste, Area Science Park, Basovizza, 34012 Trieste, Italy

and

Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, 34100 Trieste, Italy

The theoretical basis of elastic magnetic x-ray scattering is reviewed, and a detailed discussion of the physical implications of the various terms in the cross section is carried out for the non-resonant as well as for the resonant case. Relevant examples from the experimental literature are used to illustrate the general properties derived from the theoretical discussion.

I. INTRODUCTION

The purpose of this article is to review the basic aspects of (elastic) magnetic x-ray scattering, a method to investigate magnetic structures with synchrotron light, which nicely complements more traditional and widespread methods such as neutron scattering.

Although the application of magnetic x-ray scattering has only recently become popular, thanks to the development of modern synchrotron light sources, the coupling between photons and magnetic moments is predicted by quantum electrodynamics, and in fact it was described as early as 1954 by Low [1] and Gell-Mann and Goldberger [2] in their derivations of the low-energy limit of the Compton cross section. Later, Platzman and Tzoar [3] pointed out the possibility to use this effect to investigate magnetic structures.

Due to the very small cross section, it was not until 1981, however, that the first magnetic scattering experiment was carried out by de Bergevin and Brunel [4] on NiO, demonstrating the basic features of non-resonant scattering. The truly heroic aspects of this first experiment performed with an x-ray tube were later alleviated by the advent of synchrotron sources, and experiments were performed to take advantage of the attractive features of x-ray magnetic scattering, as compared to neutron scattering, i.e. the very high momentum resolution and the possibility of a separate determination of the spin and of the orbital contributions to the magnetic moment by the different polarization dependence.

A very important development took place in 1988 with the discovery by Gibbs *et al.* [5] of resonant magnetic scattering (also called resonant exchange scattering), i.e. of an enhancement of several orders of magnitude of the magnetic scattering intensity when the photon energy is close to an absorption edge of the material. A very large number of studies in rare earth, actinide and transition metal systems followed. Although the price to pay for the resonant enhancement is the loss of a direct interpretation of the scattering intensity in terms of spin and orbital magnetic structure factors, many experiments followed, and contributed to clarify many issues on the electronic structure of magnetic materials : as we shall see, the selection rules for optical transitions make the resonant process sensitive to electronic states with specific orbital character, and enhance their contribution to the magnetic properties. It is interesting to notice that the resonant scattering is sensitive not only to charge and magnetic order but also to orbital order, because the atomic scattering amplitude can vary substantially depending on the occupation of selected spin or orbital states and therefore on their availability to serve as intermediate states in the second order scattering process.

The structure of the article is the following : in Section 2 we recall the formalism necessary to set up the Hamiltonian for the interaction between radiation and matter, and to develop a perturbation description of scattering processes. In Section 3 the cross section for the non-resonant case is obtained and discussed, and the resonant case is treated in Section 4. Section 5 is devoted to final considerations and discussion of future trends.

II. INTERACTION OF RADIATION WITH ELECTRONIC MATTER

A microscopic discussion of the magnetic properties of matter, which originate from the electron spin and from quantized orbital moments, must necessarily be formulated in the language of quantum mechanics. We also need to consider relativistic effects, because quantities such as the magnetic moment associated to the electron spin appear only in a relativistic theory, and a relativistic effect such as the spin-orbit interaction plays an essential role in determining the coupling between radiation and magnetic moments, as we shall see.

We therefore expect the reader to be familiar with basic quantum mechanics and its general formalism, although more advanced topics such as relativistic quantum mechanics and the second quantization formalism are not indispensable to follow the essence of the arguments. The less experienced readers should be prepared to accept some of the intermediate steps in the calculations without a detailed proof.

In discussing the scattering of electromagnetic waves on a material system composed of electrons and nuclei, we shall follow the usual approach and consider the Hamiltonian for the material system, plus the Hamiltonian for the free electromagnetic field, plus an interaction term between the two systems. As it will be clear soon, the scattering from electrons is much more intense than the scattering from nuclei, and we shall therefore consider matter as a system of electrons, interacting with one another and with a set of nuclei in fixed positions, through a potential energy which can be written :

$$V(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N V_{nuc}(\mathbf{r}_i) + \sum_{i>j} V_C(|\mathbf{r}_i - \mathbf{r}_j|); \quad (1)$$

where the first term represents the interaction with the nuclei, and in the second the Coulomb interaction is $V_C(r) = e^2/r$. The system of electrons and nuclei is a many-body system and not much progress is possible without suitable approximations. A *self-consistent field* approximation is often introduced in which the dependence of Eq. 1 on the positions of all electrons is replaced by a one-electron average,

$$V(\mathbf{r}_1, \dots, \mathbf{r}_N) \simeq \sum_{i=1}^N V(\mathbf{r}_i). \quad (2)$$

The potential energy is the key ingredient that allows to write the Hamiltonian for the i -th electron, which, in relativistic quantum mechanics, is the Dirac Hamiltonian [6], [7]:

$$H_{el} = \sum_{i=1}^N (c\boldsymbol{\alpha} \cdot \mathbf{p}_i + \beta mc^2 + V(\mathbf{r}_i)) \quad (3)$$

where $\boldsymbol{\alpha}$ and β are the 4×4 Dirac matrices, and \mathbf{p} is the momentum four-vector (we shall soon revert to the more familiar three-dimensional notation, so the less experienced reader should not be intimidated).

The radiation field, on the other hand, is described by the electric and magnetic fields \mathbf{E}, \mathbf{B} , which obey Maxwell's equations [8], and which can also be described by introducing a scalar and a vector potential, $\Phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r}, t)$:

$$\begin{aligned} \mathbf{B} &= \nabla \times \mathbf{A} \\ \mathbf{E} &= -\nabla\Phi - (1/c)\frac{\partial \mathbf{A}}{\partial t}, \end{aligned} \quad (4)$$

where the vector $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$.

For given $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$, the definition of the vector and scalar potentials is not unique; when describing the fields of electromagnetic waves in vacuum, we can use this freedom to chose the *gauge* in such a way that the scalar potential vanishes, and the vector potential \mathbf{A} is divergence free ($\nabla \cdot \mathbf{A} = 0$) [9]. This will turn out to be a convenient choice later. An arbitrary space- and time-dependent vector potential can be expanded in terms of plane waves, which are characterized by a wavevector \mathbf{k} and by one of the two polarization modes labelled by λ . Let us write this expansion in the following form:

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\mathbf{k}, \lambda} \left(\frac{\hbar c^2}{\Omega \omega_{\mathbf{k}}}\right)^{1/2} \left[\mathbf{e}_{\lambda}(\mathbf{k}) a(\mathbf{k}, \lambda) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega_{\mathbf{k}} t)} + \mathbf{e}_{\lambda}^*(\mathbf{k}) a^{\dagger}(\mathbf{k}, \lambda) e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega_{\mathbf{k}} t)} \right]. \quad (5)$$

In this equation, Ω is the volume of the quantization box, and does not appear in any physically meaningful quantity in the following, $\omega_{\mathbf{k}}$ is just $c|\mathbf{k}|$, \mathbf{e}_{λ} is the polarization vector associated to the mode λ , i.e. one of two vectors in the plane normal to \mathbf{k} . Furthermore, in a classical description of the field, $a(\mathbf{k}, \lambda)$ and $a^{\dagger}(\mathbf{k}, \lambda)$ are the amplitude of the corresponding mode of the field and its complex conjugate. However, the reader who is familiar with the second quantization formalism knows that in this language a and a^{\dagger} are *operators*, respectively the annihilation and creation operators of a photon with quantum numbers (\mathbf{k}, λ) . In this formalism the Hamiltonian of the field takes a very simple and appealing form :

$$H_{rad} = \sum_{\mathbf{k}, \lambda} \hbar \omega_{\mathbf{k}} (a^{\dagger}(\mathbf{k}, \lambda) a(\mathbf{k}, \lambda) + 1/2). \quad (6)$$

Turning now to the modifications of H_{el} in presence of the electromagnetic field, we follow the usual prescription to insert the $\mathbf{A}(\mathbf{r}_i)$ in the Dirac Hamiltonian [6], [7]:

$$H'_{el} = \sum_{i=1}^N (c\boldsymbol{\alpha} \cdot [\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i)] + \beta mc^2 + V(\mathbf{r}_i)). \quad (7)$$

and consider that the processes we are interested in (scattering of x-ray photons in the $\sim 10keV$ range), always involve energies much smaller than the electron rest energy, $mc^2 \simeq 511keV$. This authorizes us to adopt the non-relativistic limit of Eq. 7, which is considered and derived in great detail in Section 15 of [7]. The resulting Hamiltonian, accurate to order $(1/c)^2$ is :

$$H_{el} = \sum_{i=1}^N \left[\frac{(\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i))^2}{2m} - \mathbf{p}_i^4/8m^3c^2 + V(\mathbf{r}_i) - (e\hbar/mc)\mathbf{s}_i \cdot \mathbf{B} - (e\hbar/2m^2c^2)\mathbf{s}_i \cdot (\mathbf{E} \times (\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i))) + (e/8m^2c^2)\nabla \cdot \mathbf{E} \right]. \quad (8)$$

In this equation, the first term on the r.h.s. is the usual modification of the kinetic energy in presence of a field, the second is the relativistic correction to the kinetic energy, which does not involve the field and is therefore not relevant to our discussion; the fourth term is the interaction of the electron spin $\mathbf{s} = (1/2)\hbar\boldsymbol{\sigma}$ with the magnetic field of the radiation, $\mathbf{B} = \nabla \times \mathbf{A}$; the fifth is the spin-orbit interaction term, with the usual modification of the momentum in presence of the field; and the last is the Darwin correction, which is again independent of the radiation field, because the transversality of electromagnetic waves ($\mathbf{k} \cdot \mathbf{E} = 0$) implies $\nabla \cdot \mathbf{E} = 0$, so that the only contribution to this term comes from the electric field of the charges (the gradient of V). After removing all the relativistic corrections to H'_{el} which are not affected by the radiation field, we are left with the following Hamiltonian for the system of electrons and the radiation field :

$$H = H'_{el} + H_{rad} = \sum_{i=1}^N \left[\frac{(\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i))^2}{2m} + V(\mathbf{r}_i) - (e\hbar/mc)\mathbf{s}_i \cdot \mathbf{B} - (e\hbar/2m^2c^2)\mathbf{s}_i \cdot (\mathbf{E} \times (\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i))) \right] + \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} (a^\dagger(\mathbf{k}, \lambda)a(\mathbf{k}, \lambda) + 1/2). \quad (9)$$

We are then in a position to separate all the terms mixing electron and photon variables, that constitute the *interaction Hamiltonian*, H_{int} :

$$H = H_{el} + H_{rad} + H_{int}, \quad (10)$$

$$H_{el} = \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{r}_i) + (e\hbar/2m^2c^2)\mathbf{s}_i \cdot (\nabla V(\mathbf{r}_i) \times \mathbf{p}_i) \right], \quad (11)$$

$$H_{rad} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} (a^\dagger(\mathbf{k}, \lambda)a(\mathbf{k}, \lambda) + 1/2) \quad (12)$$

$$\begin{aligned} H_{int} &= \sum_{i=1}^N [(e^2/2mc^2)\mathbf{A}^2(\mathbf{r}_i) - (e/mc)\mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i - \\ &\quad (e\hbar/mc)\mathbf{s}_i \cdot (\nabla \times \mathbf{A}(\mathbf{r}_i)) + \\ &\quad (e\hbar/2m^2c^3)\mathbf{s}_i \cdot [(\partial\mathbf{A}(\mathbf{r}_i)/\partial t) \times (\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i))] \\ &\equiv H'_1 + H'_2 + H'_3 + H'_4. \end{aligned} \quad (13)$$

The total Hamiltonian, to the required order of relativistic corrections, is thus split into the Hamiltonian for electronic matter, Eq. 11, for the radiation field, Eq. 12 and the Hamiltonian describing the interaction between matter and radiation, Eq. 13. In the next section, scattering processes will be described as transitions between the eigenstates of H_{el} and H_{rad} induced by the perturbation H_{int} . This can be done by regarding the \mathbf{A} field as a classical quantity, or alternatively and more elegantly, by considering it as an operator, according to the expansion (Eq. 5) in terms of annihilation and creation operators.

III. CROSS SECTION FOR NON-RESONANT SCATTERING

In developing the expressions for the scattering cross section, we closely follow the lucid discussion by Blume [10], warning the reader that this important paper unfortunately contains many misprints.

Our discussion is restricted to *elastic* scattering, i.e. to processes in which the sample (the system of electrons) is in the same state (for simplicity, let us say the ground state) before and after the scattering event. If we consider the scattering of an incoming photon with polarization \mathbf{e}_λ and wavevector \mathbf{k} into an outgoing photon with polarization $\mathbf{e}'_{\lambda'}$ and wavevector \mathbf{k}' (conservation of energy implies $|\mathbf{k}| = |\mathbf{k}'|$), we can describe the initial and final state of the system (sample plus radiation field) as :

$$\begin{aligned} |i\rangle &= |0; \dots, (\mathbf{e}_\lambda, \mathbf{k}), \dots\rangle; \\ |f\rangle &= |0; \dots, (\mathbf{e}'_{\lambda'}, \mathbf{k}'), \dots\rangle. \end{aligned} \quad (14)$$

with an obvious notation labelling the ground state of the electronic system with $|0\rangle$, and the radiation field state with the quantum numbers of the photons present in that state.

It is then clear that the transition consists in the *annihilation* of one photon $(\mathbf{e}_\lambda, \mathbf{k})$, and in the *creation* of one photon $(\mathbf{e}'_{\lambda'}, \mathbf{k}')$. This means that the operator \mathbf{A} , which is linear in the creation and annihilation operators, must operate twice. Therefore the lowest order contributing processes will come from applying second order perturbation theory to H'_2 and H'_3 , which contain one \mathbf{A} operator, and by first order perturbation theory applied to H'_1 and H'_4 , which contain two \mathbf{A} operators. As a matter of fact, H'_4 contains two terms, respectively proportional to $\partial\mathbf{A}/\partial t \cdot \mathbf{p}$ and to $\partial\mathbf{A}/\partial t \cdot (\epsilon/c)\mathbf{A}$. However, we shall soon verify that the second order perturbation on the first term produces a contribution to the cross section which is a factor $(\hbar\omega/mc^2)^2$ smaller than the first order contribution of the second, so we will drop it and retain the second term only.

According to Fermi's Golden Rule of time-dependent perturbation theory, the number of transitions per unit time is proportional to

$$w = \frac{2\pi}{\hbar} \left| \langle f | H'_1 + H'_4 | i \rangle + \sum_n \frac{\langle f | H'_2 + H'_3 | n \rangle \langle n | H'_2 + H'_3 | i \rangle}{E_0 - E_n + \hbar\omega_{\mathbf{k}}} \right|^2 \delta(\hbar(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})) \quad (15)$$

In the second term, the sum over the complete set of eigenstates $|n\rangle$ of the unperturbed Hamiltonian, $H_{el} + H_{rad}$ appears, referred to as the sum over the intermediate states. The calculation of the matrix elements involve both electron and photon operators and is tedious, but straightforward. For example :

$$\begin{aligned} \langle f | H'_1 | i \rangle &= \frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}} \frac{e^2}{mc^2} \sum_i \langle 0; (\mathbf{e}'_{\lambda'}, \mathbf{k}') | (\mathbf{e}'_{\lambda'} \cdot \mathbf{e}_\lambda) a^\dagger(\mathbf{k}', \lambda') a(\mathbf{k}, \lambda) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i} | 0; (\mathbf{e}_\lambda, \mathbf{k}) \rangle \\ &= \frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}} \frac{e^2}{mc^2} (\mathbf{e}'_{\lambda'} \cdot \mathbf{e}_\lambda) \sum_i \langle 0 | e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i} | 0 \rangle, \end{aligned} \quad (16)$$

after taking the photon annihilation and destruction operator matrix elements according to the usual rules. In this matrix element we recognize the *Thompson scattering* amplitude, with the dot product polarization dependence and the structure factor, expressed by the ground state expectation value of $\sum_i e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i}$. This is the basic scattering process of x-ray crystallography. In a periodic system, momentum conservation up to a reciprocal lattice vector implies the Bragg law. Notice also that the matrix element magnitude per electron is controlled by the quantity $r_0 \equiv e^2/mc^2$ which has the dimensions of length and is the Thompson radius, $r_0 = 2.818 \times 10^{-13} \text{cm}$.

We are now in a position to confirm that the scattering from the nuclei is negligible. In fact, to obtain the corresponding matrix element for nuclear scattering, we should simply replace the electronic positions with the atomic ones, and also replace e^2/mc^2 , with $Z^2 e^2/Mc^2$, where Z and M are the nuclear charge and mass. However, M is roughly proportional to $2Zm_n$, where m_n is the nucleon mass, and the mass ratio m_n/m is about 1850. Therefore, the scattering matrix element for a nucleus is $\sim Z/(2 \times 1850)$ times smaller than that for an electron, and can be neglected because Z never exceeds 92 (remember that, in addition, there are Z times more electrons than nuclei!).

To evaluate $\langle f | H'_4 | i \rangle$, we first determine an expression for the operator $\partial\mathbf{A}/\partial t$ from Eq. 5:

$$\partial\mathbf{A}/\partial t = \left(\frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)^{1/2} \left[-i\omega_{\mathbf{k}} \mathbf{e}_\lambda(\mathbf{k}) a(\mathbf{k}, \lambda) e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}}t)} + i\omega_{\mathbf{k}} \mathbf{e}'_{\lambda'}(\mathbf{k}) a^\dagger(\mathbf{k}, \lambda) e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}}t)} \right]. \quad (17)$$

Inserting this expression, the H'_4 matrix element is readily evaluated :

$$\langle f|H_4'|i\rangle = -i\left(\frac{e^2}{mc^2}\right)\left(\frac{\hbar\omega_{\mathbf{k}}}{mc^2}\right)\left(\frac{hc^2}{\Omega\omega_{\mathbf{k}}}\right)\sum_i\langle 0|e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}\mathbf{s}_i\cdot(\mathbf{e}_{\lambda'}^*(\mathbf{k}')\times\mathbf{e}_{\lambda}(\mathbf{k}))|0\rangle. \quad (18)$$

One therefore sees immediately that a term containing the spin operators, i.e. a genuine *magnetic* scattering term appears, and that its magnitude compared to the Thompson term is reduced by the factor $(\hbar\omega_{\mathbf{k}}/mc^2)$. This is a small number, because typically in the x-ray region $\hbar\omega_{\mathbf{k}} \sim 10keV$, while $mc^2 = 511keV$. We now proceed to the evaluation of the second term in Eq. 15. The accessible intermediate states have either no photons, or two photons, and their energy is :

$$|n\rangle = |\Psi_n; 0, 0\rangle; E_n = E(\Psi_n) \quad (19)$$

$$|n\rangle = |\Psi_n; (\mathbf{e}_{\lambda}, \mathbf{k}), (\mathbf{e}'_{\lambda'}, \mathbf{k}')\rangle; E_n = E(\Psi_n) + 2\hbar\omega_{\mathbf{k}} \quad (20)$$

The first set of terms (let us call them terms (a)) is reached by the action of the annihilation part of the \mathbf{A} operator on the initial state; the second (terms (b)) by the action of the creation operator part. There is also an additional, important difference between the two kinds of terms : in case (a) the energy denominator can vanish, and give rise to a resonance, when $E_0 - E_n + \hbar\omega_{\mathbf{k}} = 0$; in case (b) it cannot, because $E_0 - E(\Psi_n) - \hbar\omega_{\mathbf{k}} < 0$ always. To prevent an unphysical divergence of the scattering cross section, we must take into account that the intermediate states $|n\rangle$ are not really stationary, but have a finite lifetime, which is represented by adding a small imaginary part to the eigenvalue, which becomes important only near the resonance condition ; i.e. $E(\Psi_n)$ is replaced by $E(\Psi_n) - i\Gamma_n/2$. We want to examine the non-resonant case first, i.e. the case in which $\hbar\omega_{\mathbf{k}} \gg E(\Psi_n) - E_0$ for all states, or, more precisely, for all states $|n\rangle$ which give an appreciable contribution to the sum in Eq. 15. Using the following simple identities for the energy denominators :

$$\begin{aligned} \frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + i\Gamma_n/2} &= \frac{1}{\hbar\omega_{\mathbf{k}}} + \frac{E(\Psi_n) - E_0 - i\Gamma_n/2}{\hbar\omega_{\mathbf{k}}} \frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + i\Gamma_n/2} \\ \frac{1}{E_0 - E(\Psi_n) - \hbar\omega_{\mathbf{k}}} &= -\frac{1}{\hbar\omega_{\mathbf{k}}} + \frac{E_0 - E(\Psi_n)}{\hbar\omega_{\mathbf{k}}} \frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}}}, \end{aligned} \quad (21)$$

it is easy to see that in this case the denominators are well approximated by $\pm\hbar\omega_{\mathbf{k}}$. Substituting Eq. 5 into $H_2' + H_3'$, and paying due attention to the action of photon creation and annihilation operators on the two kinds of intermediate states, we find for type (a) intermediate states:

$$\begin{aligned} \langle f|H_2' + H_3'|n\rangle\langle n|H_2' + H_3'|i\rangle &= \\ \left(\frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)\left(\frac{e}{mc}\right)^2\langle 0|\sum_{j=1}^N[\mathbf{e}'_{\lambda'}\cdot\mathbf{p}_j - i\hbar(\mathbf{k}'\times\mathbf{e}'_{\lambda'})\cdot\mathbf{s}_j]e^{-i\mathbf{k}'\cdot\mathbf{r}_j}|n\rangle & \\ \langle n|\sum_{j'=1}^N[\mathbf{e}_{\lambda}\cdot\mathbf{p}_{j'} + i\hbar(\mathbf{k}\times\mathbf{e}_{\lambda})\cdot\mathbf{s}_{j'}]e^{i\mathbf{k}\cdot\mathbf{r}_{j'}}|0\rangle & \end{aligned} \quad (22)$$

while, for type (b) intermediate states we obtain an expression differing only in that the operators acting between $\langle 0|$ and $|n\rangle$ and between $\langle n|$ and $|0\rangle$ are interchanged. This, together with the fact that the energy denominators, in the non-resonant approximation defined above, are independent of $|n\rangle$ and change sign for the two types of intermediate states, and with the *closure* relationship :

$$\sum_n |n\rangle\langle n| = \mathbf{1} \quad (23)$$

where $\mathbf{1}$ denotes the unit operator, allows to write the second term in Eq. 15 as the expectation value of a commutator:

$$\sum_n \frac{\langle f|H_2' + H_3'|n\rangle\langle n|H_2' + H_3'|i\rangle}{E_0 - E_n + \hbar\omega_{\mathbf{k}}} \simeq \left(\frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)\left(\frac{e}{mc}\right)^2\langle 0|[C', C]|0\rangle, \quad (24)$$

where :

$$C' = [\mathbf{e}'_{\lambda'}\cdot\mathbf{p}_j - i\hbar(\mathbf{k}'\times\mathbf{e}'_{\lambda'})\cdot\mathbf{s}_j]e^{-i\mathbf{k}'\cdot\mathbf{r}_j} \quad (25)$$

$$C = [\mathbf{e}_{\lambda}\cdot\mathbf{p}_j + i\hbar(\mathbf{k}\times\mathbf{e}_{\lambda})\cdot\mathbf{s}_j]e^{i\mathbf{k}\cdot\mathbf{r}_j}. \quad (26)$$

To calculate the commutator is a tedious operation, but is easily performed remembering the basic commutation rules for components of positions, momenta, spin and arbitrary functions of them, referred to the same electron :

$$\begin{aligned} [r_\alpha, p_\beta] &= i\hbar\delta_{\alpha\beta} \\ [p_\alpha, f(\mathbf{r})] &= -i\hbar\partial f/\partial r_\alpha \\ [s_\alpha, s_\beta] &= i\hbar\epsilon_{\alpha\beta\gamma}s_\gamma. \end{aligned} \quad (27)$$

Here the antisymmetric tensor $\epsilon_{\alpha\beta\gamma}$ was introduced, and it is worthwhile to remember the expression of the cross product of two vectors in terms of it (summation over repeated indices is implied) :

$$(\mathbf{v}_1 \times \mathbf{v}_2)_\alpha = \epsilon_{\alpha\beta\gamma}v_{1\beta}v_{2\gamma}. \quad (28)$$

By a careful use of these rules, of the transversality conditions, $\mathbf{e} \cdot \mathbf{k} = 0$ and of a simple vector identity :

$$(\mathbf{A} \times \mathbf{B}) \cdot (\mathbf{C} \times \mathbf{D}) \equiv (\mathbf{A} \cdot \mathbf{C})(\mathbf{B} \cdot \mathbf{D}) - (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C}) \quad (29)$$

which is applied to the four vectors : $(\mathbf{k} - \mathbf{k}') \equiv \mathbf{q}$, \mathbf{p}_j , $\mathbf{e}'_{\lambda'}$, \mathbf{e}_λ , the patient reader should obtain :

$$\begin{aligned} \sum_n \frac{\langle f|H'_2 + H'_3|n\rangle\langle n|H'_2 + H'_3|i\rangle}{E_0 - E_n + \hbar\omega_{\mathbf{k}}} &= -i\left(\frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)\left(\frac{e^2}{mc^2}\right)\frac{\hbar\omega_{\mathbf{k}}}{mc^2} \left[\langle 0| \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \frac{i\mathbf{q} \times \mathbf{p}_j}{\hbar k^2} |0\rangle (\mathbf{e}'_{\lambda'} \times \mathbf{e}_\lambda) + \right. \\ &\left. \langle 0| \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \mathbf{s}_j |0\rangle [(\mathbf{k}' \times \mathbf{e}'_{\lambda'}) (\mathbf{k}' \cdot \mathbf{e}_\lambda) - (\mathbf{k} \times \mathbf{e}_\lambda) (\mathbf{k} \cdot \mathbf{e}'_{\lambda'}) - (\mathbf{k}' \times \mathbf{e}'_{\lambda'}) \times (\mathbf{k} \times \mathbf{e}_\lambda)] \right]. \end{aligned} \quad (30)$$

Now that we have the second order contribution of the $\mathbf{A} \cdot \mathbf{p}$ term in H'_2 , we can substantiate our claim that the contribution of the $\partial\mathbf{A}/\partial t \times \mathbf{p}$ term of H'_4 is negligible. In fact, the magnitude of the latter contribution would be similar to that of the former, which we just evaluated, except for some different prefactors. On the one hand, the time derivative introduces a factor $\omega_{\mathbf{k}}$, on the other, the constant in front of H'_4 introduces, with respect to H'_2 , another factor of $\hbar/2mc^2$, so that all in all an extra factor $\hbar\omega_{\mathbf{k}}/2mc^2$ is obtained. This shows that the matrix element of the first part of H'_4 is reduced by $(\hbar\omega_{\mathbf{k}}/2mc^2)^2$ with respect to the Thompson term, and therefore is negligible with respect to the other magnetic scattering terms, which are reduced by $\hbar\omega_{\mathbf{k}}/2mc^2$.

We are now in a position to collect all the pieces that are needed to calculate Eq. 15. However, this gives a number of transitions per unit time which depends on the normalization volume. We would rather have a physically meaningful quantity, i. e. a *cross section*, defined as : the number of transitions per unit time, into photon states with energy $\hbar\omega_{\mathbf{k}'} < E < \hbar\omega_{\mathbf{k}'} + dE$, with wavevector \mathbf{k}' in the solid angle dO' , divided by the number of incident photons per unit time and area. That is, in differential form

$$\frac{d^2\sigma}{dEdO'} = \frac{w\rho(E)}{c/\Omega} \quad (31)$$

where ρ is the density of photon states (with specified polarization), i.e. the number of wavevectors within dO' satisfying periodic boundary conditions in a box of volume Ω and $\hbar\omega_{\mathbf{k}} \leq \hbar\omega_{\mathbf{k}'} \leq \hbar\omega_{\mathbf{k}} + dE$, i.e.

$$\rho(E)dEdO' = \frac{\Omega}{(2\pi)^3} \frac{E^2}{\hbar^3 c^3} dEdO' \quad (32)$$

Finally, by putting Eq 15, 16, 18, 30, 31 together, and upon multiplying Eq. 31 by dE and integrating (remember the Dirac δ in Eq. 15) we obtain the important result in the non-resonant limit :

$$\begin{aligned} \frac{d\sigma}{dO'} &= r_0^2 \left| \sum_j \langle 0| e^{i\mathbf{q}\cdot\mathbf{r}_j} |0\rangle (\mathbf{e}'_{\lambda'} \cdot \mathbf{e}_\lambda) \right. \\ &\left. -i\frac{\hbar\omega_{\mathbf{k}}}{mc^2} \left[\langle 0| \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \frac{i\mathbf{q} \times \mathbf{p}_j}{\hbar k^2} |0\rangle \cdot \mathbf{P}_L + \langle 0| \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \mathbf{s}_j |0\rangle \cdot \mathbf{P}_S \right] \right|^2, \end{aligned} \quad (33)$$

where we introduced the polarization factors :

$$\mathbf{P}_L = (\mathbf{e}'_{\lambda'} \times \mathbf{e}_\lambda) \quad (34)$$

$$\mathbf{P}_S = [(\mathbf{k}' \times \mathbf{e}'_{\lambda'}) (\mathbf{k}' \cdot \mathbf{e}_\lambda) - (\mathbf{k} \times \mathbf{e}_\lambda) (\mathbf{k} \cdot \mathbf{e}'_{\lambda'}) - (\mathbf{k}' \times \mathbf{e}'_{\lambda'}) \times (\mathbf{k} \times \mathbf{e}_\lambda)]. \quad (35)$$

The indices L and S were adopted for these factors because the second one is attached to the term related to the spin moment, while the first pertains to a term which, as we shall show, is related to the *orbital* moment. In fact, after noting that $|\mathbf{q}| = 2|\mathbf{k}| \sin \theta_B$, where $2\theta_B$ is the scattering angle (the angle between \mathbf{k}' and \mathbf{k}), and defining $\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$, the relevant quantity can be transformed as follows :

$$\begin{aligned} \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \frac{i\mathbf{q} \times \mathbf{P}_j}{\hbar k^2} &= \frac{i}{\hbar q} (4\sin^2 \theta_B) \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \hat{\mathbf{q}} \times \mathbf{P}_j \\ &= \frac{i}{\hbar q} (4\sin^2 \theta_B) \hat{\mathbf{q}} \times \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \frac{1}{2} \sum_j [\mathbf{P}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \mathbf{P}_j] \\ &= \frac{-im}{ehq} (4\sin^2 \theta_B) \hat{\mathbf{q}} \times \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \mathbf{j}(\mathbf{r}) = \frac{-im}{ehq} (4\sin^2 \theta_B) \hat{\mathbf{q}} \times \mathbf{j}(\mathbf{q}) \end{aligned} \quad (36)$$

where the electrical current density operator $\mathbf{j}(\mathbf{r}) = (-e/2m) \sum_j [\mathbf{P}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \mathbf{P}_j]$ has been expressed in terms of the momentum and the density of electrons multiplied in symmetrized form, because they do not commute.

This current density describes the *microscopic* currents associated to the motion of the electrons, not the *macroscopic* ones, which we can assume to vanish in our system in the absence of external perturbations (remember that all matrix elements in a perturbation calculation refer to the unperturbed system eigenstates). The vanishing of macroscopic currents means that the flux across any surface S internal to the sample vanishes, i.e. :

$$\int_S \mathbf{j}(\mathbf{r}) \cdot \mathbf{n}_S dS = 0, \quad (37)$$

which implies that the microscopic current is divergence-free, i.e. $\nabla \cdot \mathbf{j}(\mathbf{r}) = 0$, and can therefore be expressed as the curl of a vector field. We write this field so that :

$$\mathbf{j}(\mathbf{r}) = c[\nabla \times \mathbf{M}_L(\mathbf{r})]. \quad (38)$$

For the purposes of our discussion, we identify $\mathbf{M}_L(\mathbf{r})$ with the density of orbital magnetization. Although a formal identification between operators is analytically involved [11], [12], one can satisfy himself of the plausibility of Eq. 38 by the classical description of magnetic fields in matter; Maxwell's equations for the fields \mathbf{H} and $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$ (no spin magnetization exists in the classical description, so here \mathbf{M} means \mathbf{M}_L) prescribe that the microscopic currents are related to the curl of \mathbf{M} by Eq. 38 (see for example [13]).

Eq. 38 implies that $\mathbf{j}(\mathbf{q}) = -ic\mathbf{q} \times \mathbf{M}_L(\mathbf{q})$. Therefore :

$$\sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \frac{i\mathbf{q} \times \mathbf{P}_j}{\hbar k^2} = \frac{mc}{ehq^2} \mathbf{q} \times [\mathbf{M}_L(\mathbf{q}) \times \mathbf{q}] \quad (39)$$

We are now ready to collect all the bits and pieces in a formula for the differential cross section :

$$\begin{aligned} \frac{d\sigma}{dO'} &= r_0^2 \left| \sum_j \langle 0 | e^{i\mathbf{q}\cdot\mathbf{r}_j} | 0 \rangle (\mathbf{e}'_{\lambda'} \cdot \mathbf{e}_\lambda) \right. \\ &\quad \left. -i \frac{\hbar\omega_{\mathbf{k}}}{mc^2} \left[\frac{mc}{eh} \langle 0 | \hat{\mathbf{q}} \times [\mathbf{M}_L(\mathbf{q}) \times \hat{\mathbf{q}}] | 0 \rangle \cdot \mathbf{P}_L + \frac{mc}{eh} \langle 0 | \mathbf{M}_S(\mathbf{q}) | 0 \rangle \cdot \mathbf{P}_S \right] \right|^2. \end{aligned} \quad (40)$$

where the polarization factor \mathbf{P}_L was redefined to include the angular factor ;

$$\mathbf{P}_L = (\mathbf{e}'_{\lambda'} \times \mathbf{e}_\lambda) 4\sin^2 \theta_B \quad (41)$$

and the Fourier transform of the *spin* magnetization density was introduced :

$$\mathbf{M}_S(\mathbf{q}) = \frac{eh}{mc} \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \mathbf{s}_j. \quad (42)$$

We are now ready to obtain from Eq. 40 the basic properties of non-resonant magnetic scattering. In a system with an ordered magnetic structure, e.g. an antiferromagnet, the densities of (orbital and spin) magnetization are periodic functions, with Fourier transforms which are non vanishing only for selected \mathbf{q} values corresponding to this periodicity. Some of these vectors may possibly coincide with reciprocal lattice vectors of the crystallographic structure, others will correspond to new reflections (*magnetic reflections*) with nonvanishing intensity below the Nel temperature, below which the antiferromagnetic order sets in.

As already noticed, the prefactor $\hbar\omega_{\mathbf{k}}/mc^2$ reduces the intensity of the magnetic terms considerably with respect to the Thompson one. To reinforce this, while all core and valence electrons contribute to Thompson scattering, only electrons in partially filled shells can contribute to magnetic scattering as the orbital and spin moments of filled shells add up to zero. Therefore, apart from the first pioneering experiments [4], the high intensity of synchrotron light sources is necessary for these experiments.

It is important to notice that \mathbf{P}_L contains the factor $4\sin^2\theta_B$, and since $|\mathbf{q}| = 2|\mathbf{k}|\sin\theta_B$, for a given reflection, i.e. for a given \mathbf{q} , $\sin\theta_B$ is proportional to $1/\hbar\omega$. Thus the weight of the orbital part decreases at high photon energies, where spin scattering dominates the magnetic cross section.

The different polarization factors \mathbf{P}_L , \mathbf{P}_S and the well known polarization properties of synchrotron radiation allow to separate the spin and the orbital contributions to the magnetic moments by changing the experimental geometry. This is a much more direct approach to the separation of the two contributions than it is possible with neutron scattering. This method was applied to rare earth systems such as Ho [5], to actinide systems such as UAs [14], [15] and more recently to 3d antiferromagnets such as NiO [16], and V_2O_3 [17]. Together with the higher momentum resolution allowed by well collimated synchrotron beams, this orbit and spin separation justifies the interest of x-ray scattering for some cases, in spite of the more widespread use of neutron scattering to determine magnetic structures.

A further important point to mention about the magnetic terms in Eq. 40 is the imaginary prefactor $-i\hbar\omega_{\mathbf{k}}/mc^2$. This means that, upon taking the square modulus, no interference of Thompson and magnetic scattering terms occurs, unless the structure factors

$$\sum_j \langle 0 | e^{i\mathbf{q}\cdot\mathbf{r}_j} | 0 \rangle \quad (43)$$

are complex (which means that the crystallographic structure is non-centrosymmetric), or that the polarization vectors are complex (corresponding to non-linear, i.e. elliptic or circular polarization). In such cases one has interference terms, and these can be useful in detecting magnetic scattering in ferromagnets [18], [19].

IV. RESONANT MAGNETIC SCATTERING

We now abandon the assumption of the non-resonant limit and consider the case in which $E(\Psi_n) - E_0 \simeq \hbar\omega_{\mathbf{k}}$, at least for one excited state Ψ_n (normally, in a solid there will be a continuum of states satisfying this condition).

Returning to the expressions of the matrix elements of $H'_2 + H'_3$ as written in Eq. 22, we want first of all to prove that the contribution of H'_2 is always much larger than that of H'_3 . To establish this, we begin by remarking that the most important excited states which are resonant with x-ray photons are those in which a core electron in one of the atoms is promoted to an empty one-electron state above the highest occupied orbital. Arguing within an approximate scheme in which the states $|0\rangle$, $|n\rangle$ are reasonably well described by an antisymmetric product of one-electron states, then the matrix elements of the operators H'_2 or H'_3 , which are sums of one-electron operators, can be written [20] in terms of an overlap integral over N-1 of the coordinates, multiplied by a one-electron matrix element, i.e:

$$\begin{aligned} \langle n | H'_2 + H'_3 | i \rangle &= \\ \left(\frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)^{1/2} \left(\frac{e}{mc}\right) \sum_{j=1}^N \langle n | [\mathbf{e}_\lambda \cdot \mathbf{p}_j + i\hbar(\mathbf{k} \times \mathbf{e}_\lambda) \cdot \mathbf{s}_j] e^{i\mathbf{k}\cdot\mathbf{r}_j} | 0 \rangle &= \\ \left(\frac{\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)^{1/2} \left(\frac{e}{mc}\right) \prod_{j=1}^{N-1} \int d\mathbf{r}_j \psi_{v_j}^{(n)*}(\mathbf{r}_j) \psi_{v_j}^{(0)}(\mathbf{r}_j) & \\ \times \int d\mathbf{r}_N \psi_{v_N}^{(n)*}(\mathbf{r}_N) [\mathbf{e}_\lambda \cdot \mathbf{p}_j + i\hbar(\mathbf{k} \times \mathbf{e}_\lambda) \cdot \mathbf{s}_j] e^{i\mathbf{k}\cdot\mathbf{r}_j} \psi_c^{(0)}(\mathbf{r}_N), & \quad (44) \end{aligned}$$

where ψ_v is a one-electron valence wavefunction, either for the ground or the n-th excited states and ψ_c a core wavefunction which is exponentially decreasing, outside an appropriate core radius r_c . We can then argue that the

main contribution to the integral comes from this inner region ; and one can see that inside this region $\mathbf{k} \cdot \mathbf{r}_j \ll 1$, for the values of $k = |\mathbf{k}|$ of interest here. This is because at the resonance condition

$$k = \omega/c = E/hc, \quad (45)$$

where E is the difference of the core and valence energy, i.e. the core ionization energy. This energy is related to the radius of the core orbital by the approximate hydrogen-like relationship :

$$E \simeq h^2/2mr_c^2 \quad (46)$$

whence one finds $r_c \simeq \hbar/\sqrt{2mE}$ and therefore

$$kr_c \simeq \sqrt{E/2mc^2}. \quad (47)$$

The right hand side is always small for all core levels, because $2mc^2$ is about 1 MeV, while the deepest core level (1s in uranium) has a binding energy of about 116 keV. So, in this most extreme case, $kr_c \simeq 0.34$, and is less for all other core levels. It is therefore legitimate, for $r \leq r_c$, to expand :

$$e^{i\mathbf{k} \cdot \mathbf{r}_j} \sim 1 + i\mathbf{k} \cdot \mathbf{r}_j - (\mathbf{k} \cdot \mathbf{r}_j)^2/2 + \dots \quad (48)$$

and to observe that the terms of the series are rapidly decreasing with increasing order (which is referred to as the multipole order). We can then reach the proof of the statement that H'_2 matrix elements dominate over those of H'_3 , i.e. that the first term in the last integral of Eq. 44 dominates over the second. The point is that for given $\psi_{vN}^{(n)}, \psi_e^{(0)}$, the lowest nonvanishing order in the series Eq. 48 for the integral of \mathbf{p}_j is lower by one than the lowest nonvanishing order for the second term (which contains the spin, but no \mathbf{r}_N operator). Remember indeed that the selection rules for atomic transitions are the same for \mathbf{p} or for \mathbf{r} matrix elements (a manifestation of the Wigner-Eckart theorem [21]), and since the H'_3 -related operator contains the spin but neither \mathbf{p} nor \mathbf{r} 's, it is necessary to have one more \mathbf{r} (with respect to the first term) in order to have a nonvanishing integral, i.e. to go to the next order in $\mathbf{k} \cdot \mathbf{r}_j$.

Therefore, near the resonance condition, the resonant terms dominate the cross section, and, among these, only the H'_2 matrix elements need to be retained. Eq. 15 becomes :

$$w = \frac{2\pi}{\hbar} \left| \sum_n \frac{\langle f|H'_2|n\rangle \langle n|H'_2|i\rangle}{E_0 - E_n + \hbar\omega_{\mathbf{k}} + i\Gamma_n/2} \right|^2 \delta(\hbar(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})) = \frac{2\pi}{\hbar} \left| \left(\frac{hc^2}{\Omega\omega_{\mathbf{k}}} \right) \left(\frac{e}{mc} \right)^2 \sum_n \frac{\langle 0 | \sum_{j=1}^N \mathbf{e}'_{\lambda'} \cdot \mathbf{p}_j e^{-i\mathbf{k}' \cdot \mathbf{r}_j} | n \rangle \langle n | \sum_{j'=1}^N \mathbf{e}_{\lambda} \cdot \mathbf{p}_{j'} e^{i\mathbf{k} \cdot \mathbf{r}_{j'}} | 0 \rangle}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + i\Gamma_n/2} \right|^2 \delta(\hbar(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})) \quad (49)$$

As a matter of fact, the above equation contains a contribution that was already taken into account in the non-resonant part ; remember Eq. 21, where the first piece on the r.h.s. was included in the previous Section. Therefore, only the second addendum needs to be considered here and that means that in Eq. 49 we must replace :

$$\frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + i\Gamma_n/2} \quad (50)$$

with :

$$\frac{E(\Psi_n) - E_0 - i\Gamma_n/2}{\hbar\omega_{\mathbf{k}}} \frac{1}{E_0 - E(\Psi_n) + \hbar\omega_{\mathbf{k}} + i\Gamma_n/2} \quad (51)$$

Let us then look in detail into the relevant matrix elements. Consider :

$$\langle n | \mathbf{e}_{\lambda} \cdot \mathbf{p}_j e^{i\mathbf{k} \cdot \mathbf{r}_j} | 0 \rangle \simeq \langle n | \mathbf{e}_{\lambda} \cdot \mathbf{p}_j (1 + i\mathbf{k} \cdot \mathbf{r}_j + \dots) | 0 \rangle \quad (52)$$

and, for a given $|n\rangle$, consider only the lowest order term for which the matrix element does not vanish. We established already that all higher order terms are negligible in comparison to it. The largest contributions come from those $|n\rangle$'s for which the first term provides a nonvanishing contribution, so that the exponential is simply replaced by 1. These states are said to be accessible by *electric dipole* transitions. In a full quantum electrodynamical formulation, one can see that electric dipole transitions are induced by photons with a total angular momentum of 1. The name *electric dipole* comes from the fact that in a non-relativistic theory, neglecting the spin-orbit interaction altogether, so that $H_{el} = \sum_j (\mathbf{p}_j^2/2m + V(\mathbf{r}_j))$, one can write :

$$\begin{aligned}\langle n|\mathbf{e}_\lambda \cdot \mathbf{p}_j|0\rangle &= m\langle n|\mathbf{e}_\lambda \cdot \dot{\mathbf{r}}_j|0\rangle = \frac{-im}{\hbar}\langle n|\mathbf{e}_\lambda \cdot [\mathbf{r}_j, H_{el}]|0\rangle = \\ &= \frac{im}{\hbar}[E(\Psi_n) - E(0)]\langle n|\mathbf{e}_\lambda \cdot \mathbf{r}_j|0\rangle.\end{aligned}\quad (53)$$

In view of this, and neglecting $i\Gamma_n/2$ in the numerator of Eq. 51, the sum over intermediate states in Eq. 49 becomes :

$$\frac{m^2}{\hbar^2} \sum_n \frac{(E(\Psi_n) - E(0))^3}{h\omega_{\mathbf{k}}} \frac{\langle 0|\mathbf{e}'_{\lambda'} \cdot \mathbf{R}|n\rangle\langle n|\mathbf{e}_\lambda \cdot \mathbf{R}|0\rangle}{E(\Psi_n) - E(0) + h\omega_{\mathbf{k}} + i\Gamma_n/2}, \quad (54)$$

where we defined

$$\mathbf{R} = \sum_j \mathbf{r}_j. \quad (55)$$

In order to make progress and to make contact with the literature [22], we express all vectors in terms of their *spherical* components, i.e. we define :

$$R_0 = iR_z, R_{\pm 1} = (\mp i/\sqrt{2})(R_x \pm iR_y). \quad (56)$$

The definitions of the $0, \pm 1$ components apply to any vector, e.g. to the polarization \mathbf{e}_λ as well, and they are clearly inspired from the definition of the spherical harmonics for $l = 1$,

$$Y_{1,0} = i\sqrt{\frac{3}{4\pi}}(z/r), Y_{1,\pm 1} = \mp i\sqrt{\frac{3}{8\pi}}\left(\frac{x \pm iy}{r}\right), \quad (57)$$

where we adopted the convention for the phases given in ref. [23]. It is easily verified that the scalar product becomes :

$$\mathbf{e}_\lambda \cdot \mathbf{R} = \sum_{m=-1}^1 (-1)^{m-1} e_m R_{-m}. \quad (58)$$

It is then easy to see that :

$$\langle 0|\mathbf{e}'_{\lambda'} \cdot \mathbf{R}|n\rangle\langle n|\mathbf{e}_\lambda \cdot \mathbf{R}|0\rangle = \sum_{m,m'} (-1)^{m+m'} e'^*_{\lambda'm} e_{\lambda m'} \langle 0|R_{-m}|n\rangle\langle n|R_{-m'}|0\rangle. \quad (59)$$

To simplify this expression further, one must take advantage of the symmetry of the physical system. The simplest case corresponds of course to the highest symmetry, i.e. the spherical symmetry of isolated atoms. Then, the eigenstates $|0\rangle$ and $|n\rangle$ are eigenstates of the angular momentum and of its z-component, and this implies that the sum is restricted to $m = -m'$, because the angular momentum selection rules say that, for the matrix elements :

$$\begin{aligned}\langle 0|R_{-m}|n\rangle \neq 0 &\Rightarrow -m_0 - m + m_n = 0, \\ \langle n|R_{-m'}|0\rangle \neq 0 &\Rightarrow -m_n - m' + m_0 = 0, \\ &\Rightarrow m = -m'\end{aligned}\quad (60)$$

The sum in Eq. 59 is then simplified and it is worth noticing that :

$$\begin{aligned}\langle 0|R_0|n\rangle\langle n|R_0|0\rangle &= -|\langle n|R_0|0\rangle|^2 \\ \langle 0|R_{-1}|n\rangle\langle n|R_1|0\rangle &= |\langle n|R_1|0\rangle|^2 \\ \langle 0|R_1|n\rangle\langle n|R_{-1}|0\rangle &= |\langle n|R_{-1}|0\rangle|^2\end{aligned}\quad (61)$$

The first relationship may look surprising, but remember that, because of the factor i in the definition, coming from the chosen convention on the phases of the spherical harmonics, R_0 is an antihermitian operator. Another consequence of that is the fact that if

$$e_{\lambda 0} = ie_{\lambda z} \quad (62)$$

it is also

$$e^*_{\lambda 0} = ie^*_{\lambda z}, \quad (63)$$

i.e. the spherical component 0 of the complex conjugate need not be the complex conjugate of the 0 component. With the help of all of the above we can write :

$$\begin{aligned} \langle 0 | e'^*_{\lambda'} \cdot \mathbf{R} | n \rangle \langle n | \mathbf{e}_\lambda \cdot \mathbf{R} | 0 \rangle &= -e'^*_{\lambda' 0} e_{\lambda 0} |\langle n | R_0 | 0 \rangle|^2 + e'^*_{\lambda' 1} e_{\lambda -1} |\langle n | R_1 | 0 \rangle|^2 \\ &\quad + e'^*_{\lambda' -1} e_{\lambda 1} |\langle n | R_{-1} | 0 \rangle|^2. \end{aligned} \quad (64)$$

Going back to cartesian coordinates for the polarization vectors, it is possible, with a bit of algebra to recast this expression in the following form :

$$\begin{aligned} e'^*_{\lambda' z} e_{\lambda z} [|\langle n | R_0 | 0 \rangle|^2 - \frac{1}{2} (|\langle n | R_1 | 0 \rangle|^2 - |\langle n | R_{-1} | 0 \rangle|^2)] &+ \\ \frac{1}{2} \mathbf{e}'^*_{\lambda'} \cdot \mathbf{e}_\lambda (|\langle n | R_1 | 0 \rangle|^2 + |\langle n | R_{-1} | 0 \rangle|^2) & \\ - \frac{i}{2} (\mathbf{e}'^*_{\lambda'} \times \mathbf{e}_\lambda)_z (|\langle n | R_1 | 0 \rangle|^2 - |\langle n | R_{-1} | 0 \rangle|^2). & \end{aligned} \quad (65)$$

We define :

$$F^e_{1,m} = m_e \sum_n \frac{E(\Psi_n) - E(0)}{h^3 \omega_{\mathbf{k}}} \frac{|\langle n | R_m | 0 \rangle|^2}{E(0) - E(\Psi_n + h\omega_{\mathbf{k}} + i\Gamma_n/2)} \quad (66)$$

where the label e and 1 on F remind us that this refers to electric (e) dipole ($l=1$) contributions, and where we introduced the symbol m_e for the electron mass, to avoid any confusion with the index m , which runs over $0, \pm 1$; reinserting the prefactors present in Eq. 49 and those allowing to relate w to $d\sigma/dO'$, see Eq. 31, we finally obtain:

$$\frac{d\sigma}{dO'} = |f_{res}|^2, \quad (67)$$

where f_{res} is the resonant scattering *amplitude*, given by :

$$\begin{aligned} f_{res} &= -r_0 \left[\frac{1}{2} \mathbf{e}'^*_{\lambda'} \cdot \mathbf{e}_\lambda (F^e_{1,1} + F^e_{1,-1}) \right. \\ &\quad \left. - \frac{i}{2} (\mathbf{e}'^*_{\lambda'} \times \mathbf{e}_\lambda) \cdot \hat{\mathbf{z}} (F^e_{1,1} - F^e_{1,-1}) \right. \\ &\quad \left. + (\mathbf{e}'^*_{\lambda'} \cdot \hat{\mathbf{z}}) (\mathbf{e}_\lambda \cdot \hat{\mathbf{z}}) (F^e_{1,0} - \frac{1}{2} F^e_{1,1} - \frac{1}{2} F^e_{1,-1}) \right], \end{aligned} \quad (68)$$

where the unit vector in the z direction (i.e. in the axis of quantization of the angular momenta), $\hat{\mathbf{z}}$, was introduced. Eq. 68 was derived in [22] using the relativistic formalism of vector spherical harmonics, soon after the discovery of resonant magnetic scattering by Gibbs *et al.* [5]. A more complicated expression can also be derived for electric quadrupole transitions, i.e. for the case in which the resonant transitions are only allowed if the second term in the expansion of $e^{i\mathbf{k}\cdot\mathbf{r}} \simeq 1 + i\mathbf{k}\cdot\mathbf{r} + \dots$ is retained (see for example [24]). Dipole and quadrupole terms allowed a detailed interpretation of the experiments of Gibbs *et al.* on holmium, a rare earth with a spiral antiferromagnetic phase in the $20K \leq T \leq 131K$ temperature range.

As we emphasized before, Eq. 68 was derived under the assumption of a system with spherical symmetry, for example a single magnetic ion in a weak (i.e. negligible) crystal field environment. This is a reasonable approximation for rare earth ions, in which the magnetic f shell is very localized and does not hybridize at all with the orbitals of the surrounding atoms.

The three terms in Eq. 68 describe resonant or anomalous scattering in general, not only in the magnetic case, and the three terms are therefore rather different in nature. The first is proportional to $(F^e_{1,1} + F^e_{1,-1})$ and is therefore nonvanishing even for a completely isotropic system, with no magnetic moment selecting a particular direction. It is related to pure charge scattering. The second is a genuinely magnetic term, because it originates from the difference between the 1 and the -1 components, which arise only in the presence of a magnetic preference for one direction along the quantization axis. Finally, the last term is nonvanishing for any anisotropic system, a system with a preferential axis, identified either by a crystal anisotropy or by a magnetic moment.

At the location of each ion, the quantization direction $\hat{\mathbf{z}}$ coincides with the direction of the magnetic moment. The existence of an ordered magnetic structure means that there is a dependence on the ion lattice position of the type

$$\hat{z}_i(\mathbf{R}_{lmn}) = \hat{z}_i(0,0,0) \sum_h a_i(\mathbf{K}_h) e^{i\mathbf{K}_h \cdot \mathbf{R}_{lmn}}, \quad (69)$$

where $i = x, y, z$; (l, m, n) are integers labelling the lattice sites, and the set of wavevectors \mathbf{K}_h characterise the structure. The scattering amplitude f_{res} derived above is for an ion sitting at the origin; for an ion sitting at \mathbf{R}_{lmn} it acquires a factor $e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_{lmn}}$ (by replacing \mathbf{r}_j with $\mathbf{r}_j + \mathbf{R}_{lmn}$ in Eq. 49) and, of course, one must replace $\hat{\mathbf{z}}(0,0,0)$ with $\hat{\mathbf{z}}(\mathbf{R}_{l,m,n})$. These replacements, together with Eq. 69 guarantee that when the contribution of all sites is added up, a nonvanishing intensity is obtained only if the scattering vector $\mathbf{k} - \mathbf{k}'$ equals one of the \mathbf{K}_h vectors of the magnetic structure.

If the assumption of spherical symmetry is untenable, as it is the case for 3d systems, for which the interaction with the environment results in strong crystal field effects, the selection rules on m, m' are modified, producing more complicated expressions, which are exemplified, for some point group symmetries, in [24].

The reader may wonder where, in the formulation in terms of dipole transitions between the ground and the intermediate states, the sensitivity to magnetic moments may come from. This is a subtle but very important point. In fact, no spin operators appear in the resulting expressions. The sensitivity to magnetic moments comes from the combined action of two ingredients: the Pauli principle and the spin-orbit interaction. The Pauli principle enters because of the strong dependence of the scattering amplitude on the availability of states, at or near the resonance energy, suitable to play the role of intermediate states. In a one-electron language, if states with a given spin are predominantly occupied, this implies that it is mostly states with the opposite spin which are available to be virtually filled by the promotion of a core electron in the first part of the resonant scattering process. Since the spin is conserved in the optical transition, it is mostly electrons with the same spin as the predominantly available intermediate states which are virtually excited. In the case of all core levels with $l \neq 0$, the spin-orbit interaction is nonvanishing and much larger than in the valence states (for example, the L_2 and L_3 core levels of the rare earths are separated by many hundreds of eV). In a given spin-orbit partner, states with spin up or down have a different orbital character (the spin *polarizes* the orbital state, i.e. it tends to line up the orbital moment along or against the spin direction). Because of the dipole selection rules to the available intermediate states, this orbital polarization translates into a difference between the transition rates for different m , therefore in an imbalance among the corresponding $F^e_{1,m}$, which is in turn responsible for a nonvanishing magnetic scattering amplitude.

The above qualitative description must be modified for s core levels, which have a vanishing spin-orbit interaction. In this case, resonant magnetic scattering is also observable [25], but it must be ascribed to the much weaker spin-orbit interaction of the valence states, which acts to polarize the final states of given spin and to reproduce the same mechanism.

V. CONCLUSIONS

In the preceding sections, an overview of the theoretical foundations of x-ray magnetic scattering was attempted. The purpose was to a large extent pedagogical, trying to adopt the simplest possible arguments to arrive at an understanding of the information and of the quantities accessible to this experimental technique.

There is at present an ongoing effort to explore new magnetic materials, magnetic microstructures and materials with strong electronic correlations by x-ray scattering, in particular by resonant scattering. This technique has the added value of atomic specificity (an important asset when dealing with systems with more than one magnetic element), and even the specific sensitivity to the electronic shell of the atom, via the selection rules and the choice of the energy. It has originally found applications in the hard x-ray regime, and more recently in the soft x-ray regime, especially in connection to artificial structures (multilayers and superlattices) with periods much longer than atomic distances.

Materials with strong electronic correlations, which are very central in contemporary condensed matter research, are characterized by the interplay of structural, electronic and magnetic properties. In some cases, long range ordered arrangements of spins, of charge and of orbital symmetry coexist, such as in the case of $La_{0.5}Ca_{0.5}MnO_3$ or $La_{0.5}Sr_{1.5}MnO_4$. Resonant scattering from the Mn K-edge is to some extent sensitive to all these kinds of order parameters and has therefore been used to investigate them [26]. Another system of interest is V_2O_3 , where magnetic and orbital order have been investigated by resonant scattering at the V K-edge [27].

It seems therefore easy to predict an intense activity in the field in the next few years, stimulated by the progress in synchrotron radiation sources with tunable polarization properties and by the opportunities offered by resonant scattering in the investigation of some very interesting physical systems. It is also to be expected that some of the results, as it happened already in the case of Ref. [26], [27], will stimulate a lively theoretical activity.

- [1] F.E. Low, Phys. Rev. **96**, 1428(1954)
- [2] M. Gell-Mann and M.L. Goldberger, Phys. Rev. **96**, 1433(1954)
- [3] P. Platzman and N. Tzoar, Phys Rev. **B2**, 3556(1970)
- [4] F. de Bergevin and M. Brunel, Acta Cryst. **A37**, 314(1981)
- [5] D. Gibbs, D.R. Harshman, E.D. Isaacs, D.B. McWhan, D. Mills and C. Vettier, Phys. Rev. Lett. **61**, 1241(1988)
- [6] V.B. Berestetskii, E.M. Lifshitz and L.P. Pitaevskii, *Quantum Electrodynamics*, 2nd edition (Reed, Oxford, 1982), section 21.
- [7] A.I. Akhiezer and V.B. Berestetskii, *Quantum Electrodynamics*, (Wiley, New York, 1965), Sections 12 and 15.
- [8] J.D. Jackson, *Classical Electrodynamics*, 2nd edition (Wiley, New York, 1975), section 6.3.
- [9] L.D. Landau and E.M. Lifshitz, *The Classical Theory of Fields*, 4 th edition (Reed, Oxford, 1975), section 46.
- [10] M. Blume, J. Appl. Phys. **57**, 3615 (1985)
- [11] G. Trammel, Phys. Rev. **92**, 1387 (1953)
- [12] G. Steinsvoll *et al.*, Phys. Rev. **161**, 499 (1963)
- [13] L.D. Landau and E.M. Lifshitz, *Electrodynamics of Continuous Media*, 2nd edition (Reed, Oxford, 1984), section 29, pp. 105-107
- [14] D.B. McWhan *et al.*, Phys. Rev B**42**, 6007 (1990)
- [15] S. Langridge *et al.*, Phys. Rev. **B55**, 6392 (1997)
- [16] V. Fenandez, C. Vettier, F de Bergevin, C. Giles and W. Neubeck, Phys. Rev. **B57**, 7870 (1998)
- [17] L. Paolasini *et al.*, to be published.
- [18] M. Brunel, G. Patrat, F. de Bergevin, F. Rousseaux and M. Lemonnier, Acta Cryst. **A39**, 84 (1983)
- [19] D. Laundy, S.P. Collins and A.J. Rollason, J. Phys. : Condens. Matter **3**, 369 (1991)
- [20] see e.g. S. Raimes *Many-Electron Theory*, (North Holland, Amsterdam, 1972)
- [21] see e.g. A.R. Edmonds, *Angular Momentum in Quantum Mechanics*, (Princeton University Press, Princeton, 1957)
- [22] J.P. Hannon, G.T. Trammel, M. Blume and D. Gibbs, Phys. Rev. Lett. **61**, 1245 (1988) ; *ibid.* (E) **62**, 2644 (1989).
- [23] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, 3 rd edition (Reed, Oxford, 1977), Appendix c.
- [24] J.P. Hill and D.F. McMorrow, Acta Crystallog. A**52**, 10336 (1996).
- [25] see for example W. Neubeck, C. Vettier, K.B. Lee and F. de Bergevin, Phys. Rev. **B60**, R9912 (1992) ; A. Stunault, F. de Bergevin, D. Wermeille, C. Vettier, Th. Brckel, N. Bernhoeft, G. J. McIntyre and J. Y. Henry, Phys. Rev. **B60**, 10170 (1999).
- [26] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **80**, 1932 (1998)
- [27] L. Paolasini, C. Vettier, F. de Bergevin, F. Yakhou, D. Mannix, A. Stunault, W. Neubeck, M. Altarelli, M. Fabrizio, P. A. Metcalf, and J. M. Honig, Phys. Rev. Lett. **82**, 4719 (1999).

Introduction to X-ray Magnetic Scattering

M. Altarelli

- 1. Why magnetic x-ray scattering? How?**
- 2. Non-Resonant and Resonant Scattering**
- 3. Examples with Hard and Soft X-rays**

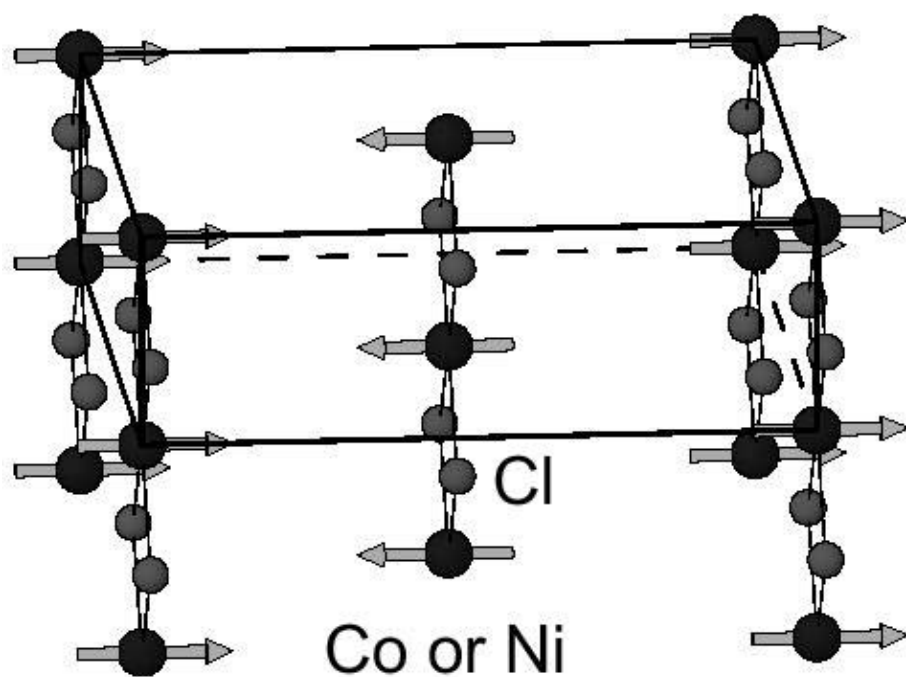


Fig. 4. Magnetic structure of $MCl_2(bpy-d8)$, $M = Co$ and Ni , below 5.0 or 8.5 K, respectively. The origin of the unit cell is shifted to $(\frac{1}{4}, \frac{1}{4}, 0)$. Only metal and Cl atoms are shown

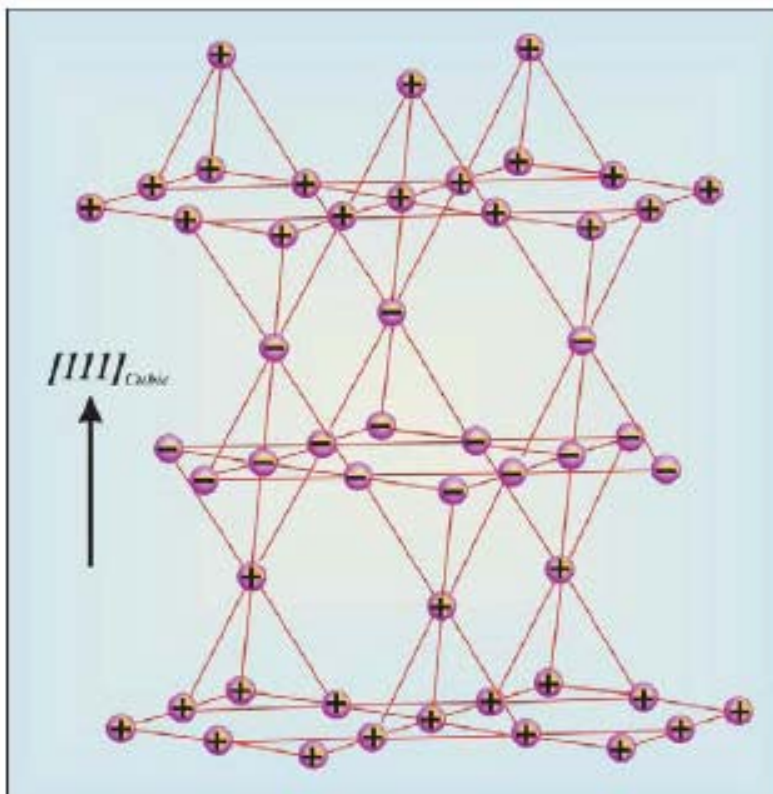
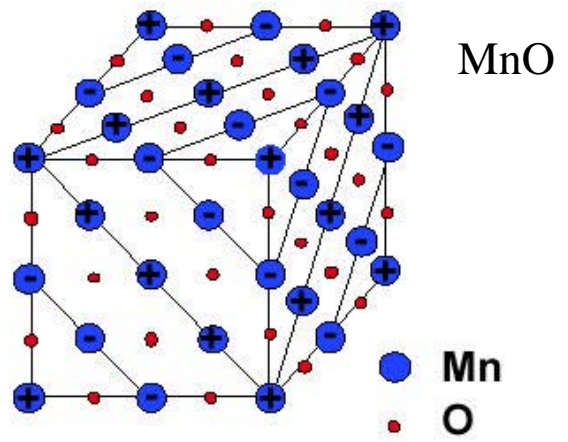
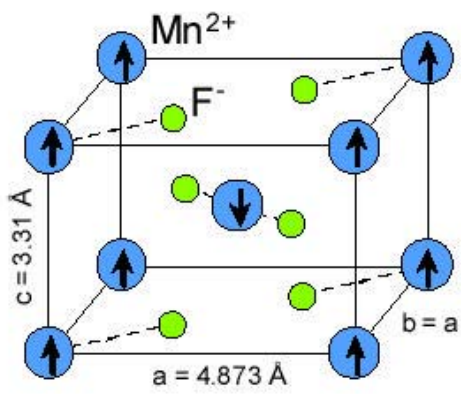
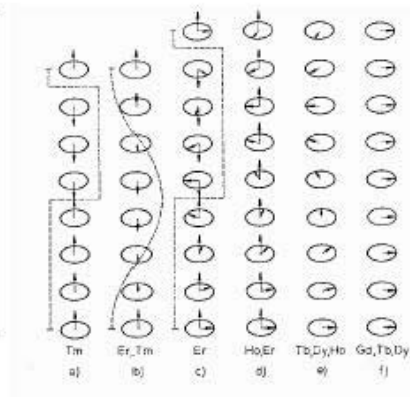
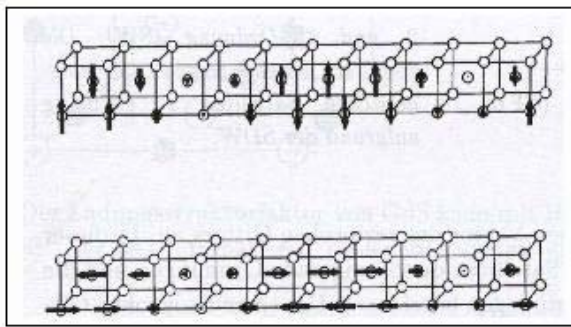


Fig. 1. A view of the crystal structure of GeNi_2O_4 , illustrating the magnetically frustrated corner-sharing tetrahedra. The relative Ni^{2+} spin directions are shown by the plus and minus signs for the two collinear magnetic sublattices.

MnF₂



Cr



Determination of Magnetic Structures

NEUTRON SCATTERING is the standard probe for structure determination

X-RAY SCATTERING useful in special cases:

Small samples

High momentum space resolution (periods of incommensurate structures)

ORBITAL-SPIN separation (non-resonant)

Presence of more than one magnetic element (resonant)

Consider a system of electrons moving in the field of the nuclei, $V_N(\vec{r}_i)$ and interacting with one another via a Coulomb potential $V_c(|\vec{r}_i - \vec{r}_j|)$, described by the Hamiltonian:

$$\hat{H} = \sum_{ji} \frac{\vec{p}_i^2}{2m} + V_N(\vec{r}_i) + V_c(|\vec{r}_i - \vec{r}_j|) + (e\hbar / 2m^2 c^2) \vec{s}_i \cdot (\nabla V(\vec{r}_i) \times \vec{p}_i)$$

The last term is the *Spin-Orbit* interaction.

Simplify this many-body Hamiltonian by somehow making an average potential for each electron:

$$\hat{H} = \sum_i \frac{\vec{p}_i^2}{2m} + V(\vec{r}_i) + (e\hbar / 2m^2 c^2) \vec{s}_i \cdot (\nabla V(\vec{r}_i) \times \vec{p}_i)$$

Remember that every electron carries a spin 1/2 and a magnetic moment:

$$\vec{\mu}_i = (e\hbar / mc) \vec{s}_i$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

$$\mathbf{E} = -\nabla\Phi - (1/c)\frac{\partial\mathbf{A}}{\partial t},$$

Fields \mathbf{E} , \mathbf{B} from potentials \mathbf{A} , Φ

where the vector $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$.

To describe electromagnetic waves, we can choose a gauge where the scalar potential $\Phi=0$, and the vector potential is:

$$\vec{A}(\vec{r}, t) = \sum_{\vec{k}, \lambda} \left(\frac{he^2}{\Omega\omega_k} \right)^{1/2} [\vec{e}_\lambda a(\vec{k}, \lambda) e^{i(\vec{k} \cdot \vec{r} - \omega_k t)} + c.c.]$$

Normal.
Box Volume

Polarization
vector $\lambda=1,2$

$\omega_k = ck$

General recipe (from classical physics) to introduce interaction of electrons with field $\mathbf{A}(\mathbf{r},t): \mathbf{p} \Rightarrow \mathbf{p} - (e/c)\mathbf{A}$.
 Also: do not forget interaction of magnetic moment μ with magnetic field of radiation:

Kinetic Energy

$\mu \cdot \mathbf{B}$

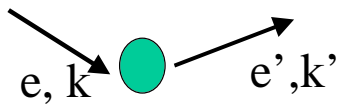
$$\hat{H} = \sum_{i=1,N} \left[\frac{(\vec{p}_i - (e/c)\vec{A}(\vec{r}_i))^2}{2m} + V(\vec{r}_i) - (e\hbar/mc)\vec{s}_i \cdot \vec{B} - (e\hbar/2m^2c^2)\vec{s}_i \cdot (\vec{E} \times (\vec{p}_i - (e/c)\vec{A}(\vec{r}_i))) \right]$$

Spin-Orbit

$$\begin{aligned}
H_{int} = & \sum_{i=1}^N \left[\overset{\mathbf{H}_1}{(e^2/2mc^2)\mathbf{A}^2(\mathbf{r}_i)} - \overset{\mathbf{H}_2}{(e/mc)\mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i} - \right. \\
& \overset{\mathbf{H}_3}{(e\hbar/mc)\mathbf{s}_i \cdot (\nabla \times \mathbf{A}(\mathbf{r}_i))} + \\
& \left. \overset{\mathbf{H}_4}{(e\hbar/2m^2c^3)\mathbf{s}_i \cdot [(\partial\mathbf{A}(\mathbf{r}_i)/\partial t) \times (\mathbf{p}_i - (e/c)\mathbf{A}(\mathbf{r}_i))]} \right]
\end{aligned}$$

We already encountered H_1 and H_2 . There are two new terms, H_3 and H_4 , that are related to the *electron spin*

Elastic Scattering Processes



This photon present in the initial state

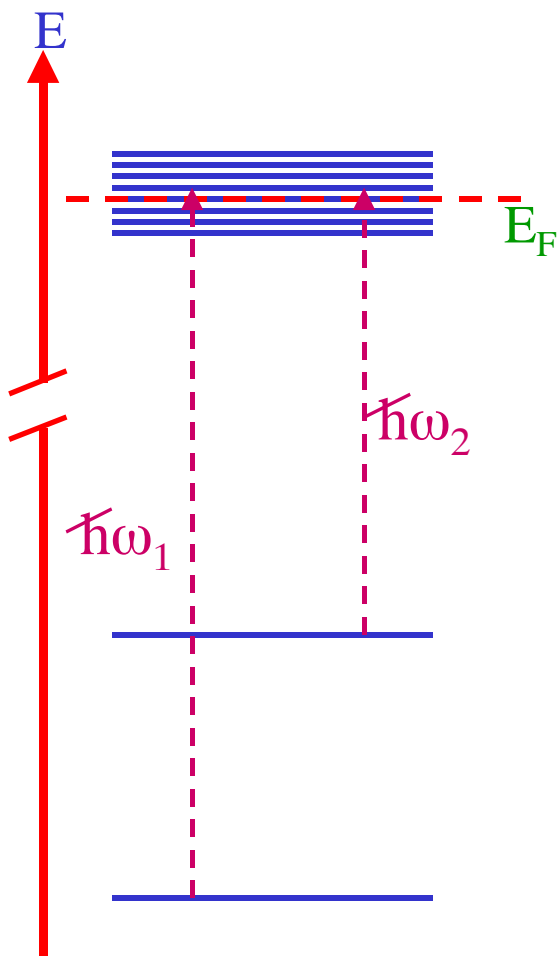
$$|i\rangle = |0; \dots, (\mathbf{e}_\lambda, \mathbf{k}), \dots\rangle;$$
$$|f\rangle = |0; \dots, (\mathbf{e}'_{\lambda'}, \mathbf{k}'), \dots\rangle$$

Electronic ground state

This photon present in the final state

We saw in a previous lecture how H_1 gives origin to **Thompson scattering**. Including the three other pieces gives additional terms that can be derived in detail.

Before describing them we must discuss the difference between **non-resonant** and **resonant** scattering.



A

Non-resonant:
 $\hbar\omega \gg \hbar\omega_1, \hbar\omega_2$

B

Resonant:
 $\hbar\omega \cong \hbar\omega_1$
 OR
 $\hbar\omega \cong \hbar\omega_2$

A

In the non-resonant case $(\hbar\omega \gg \hbar\omega_1, \hbar\omega_2)$

all of the 4 terms contribute

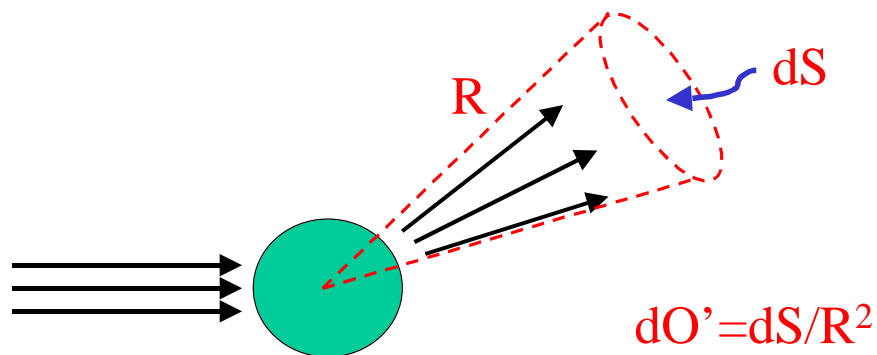
B

In the resonant case $(\hbar\omega \cong \hbar\omega_1 \text{ or } \hbar\omega \cong \hbar\omega_2)$

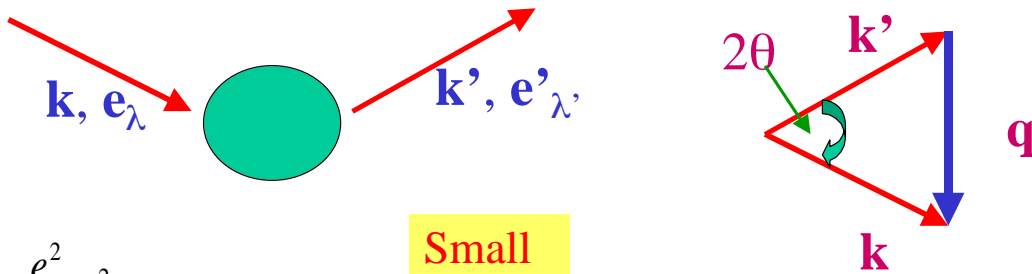
the term $H_2 = (e/mc) \Sigma \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i$ dominates all others

The quantity that best describes the intensity of the elastic scattering is the differential cross section:

$$\frac{d\sigma}{d\Omega'} = \frac{\text{Number of photons per unit time scattered within } d\Omega'}{\text{Number of incident photons per unit time per unit surface}}$$



A Non-resonant scattering



$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 \cdot$$

Small factor!

$$\left| \sum_j \langle 0 | e^{i\vec{q}\cdot\vec{r}_j} | 0 \rangle (\vec{e}'^*_\lambda \cdot \vec{e}_\lambda) - i \frac{\hbar\omega_{\vec{k}}}{mc^2} \left[\frac{mc}{e\hbar} \langle 0 | \hat{q} \times [\vec{M}_L(\vec{q}) \times \hat{q}] | 0 \rangle \cdot \vec{P}_L + \frac{mc}{e\hbar} \langle 0 | \vec{M}_S(\vec{q}) | 0 \rangle \cdot \vec{P}_S \right] \right|^2$$

Thompson
(charge scattering)

F.T. of *orbital*
moment density

F.T. of *spin*
moment density

90° dephasing

A Non-resonant scattering

Definitions:

$$\hat{q} = \frac{\vec{q}}{q}$$

$$\vec{M}_L(\vec{q}) = \sum_i e^{i\vec{q}\cdot\vec{r}_i} \vec{M}_L(\vec{r}_i)$$

$$\vec{M}_S(\vec{q}) = \sum_i e^{i\vec{q}\cdot\vec{r}_i} \vec{s}_i$$

$$\vec{P}_L = (\vec{e}' *_{\lambda} \times e_{\lambda}) 4 \sin^2 \theta$$

$$\vec{P}_S = [(\vec{k}' \times \vec{e}' *_{\lambda'}) (\vec{k}' \cdot \vec{e}_{\lambda}) - (\vec{k} \times \vec{e}_{\lambda}) (\vec{k} \cdot \vec{e}' *_{\lambda'}) - (\vec{k}' \times \vec{e}' *_{\lambda'}) \times (\vec{k} \times \vec{e}_{\lambda})]$$

A Non-resonant scattering

1. Is very weak compared to Thompson scattering

$$\left(\frac{\hbar\omega}{mc^2}\right)^2 \cong \left(\frac{10keV}{511keV}\right)^2 \cong \frac{1}{2500}$$
$$N_{mag} < Z$$

2. Has a very different polarization factor for orbital M_L and spin M_S components of the magnetic moment. Therefore selecting the incoming photon polarization and analyzing the outgoing photon polarization one can see either “orbital” or “spin” scattering

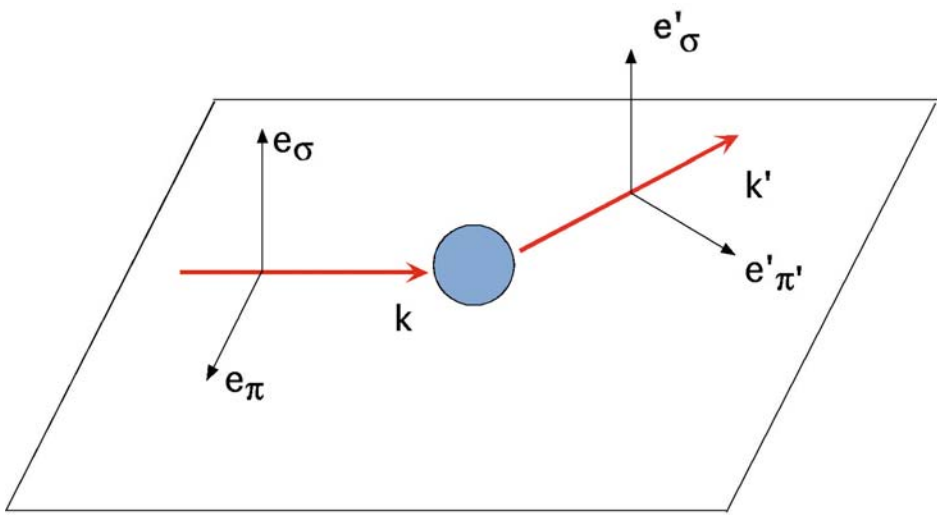


Fig. 1a

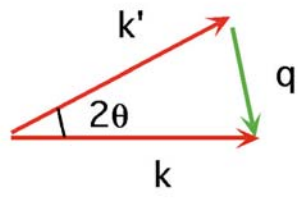
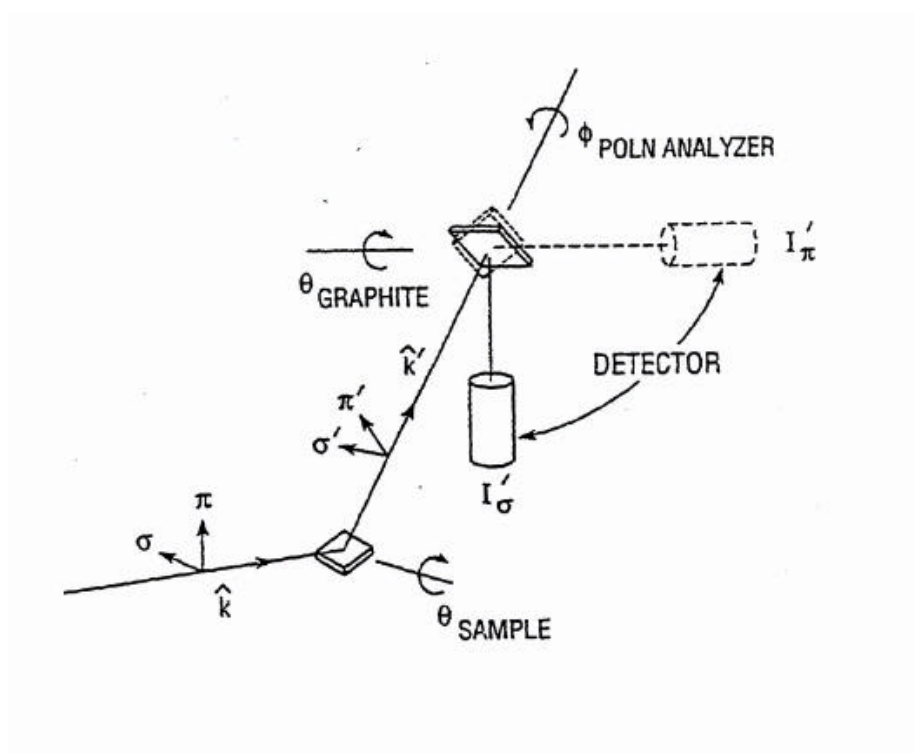
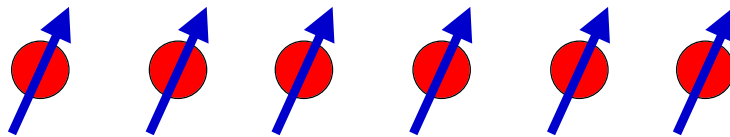


Fig. 1b



Analysis of polarization by 90° scattering on a “poor” crystal

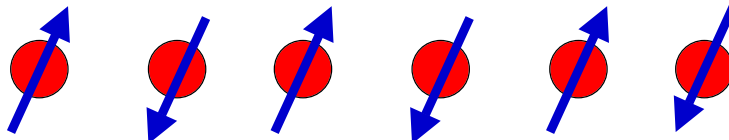
Observation of Magnetic X-ray Scattering



Ferromagnet : magnetic periodicity=lattice periodicity



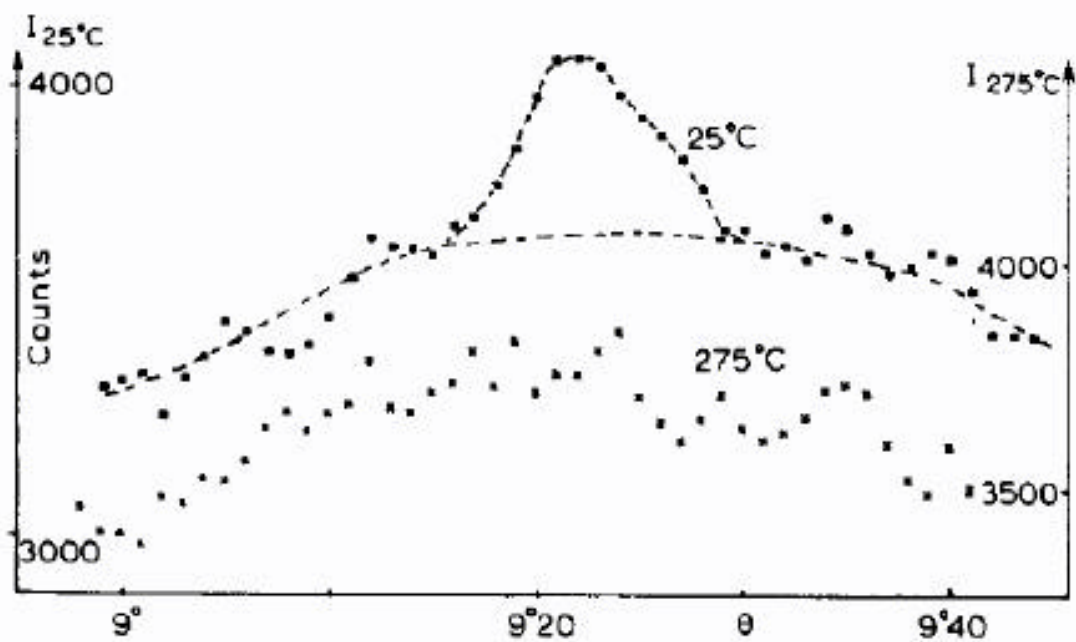
Same reciprocal lattice vectors



Antiferromagnet : magnetic periodicity= multiple of lattice periodicity

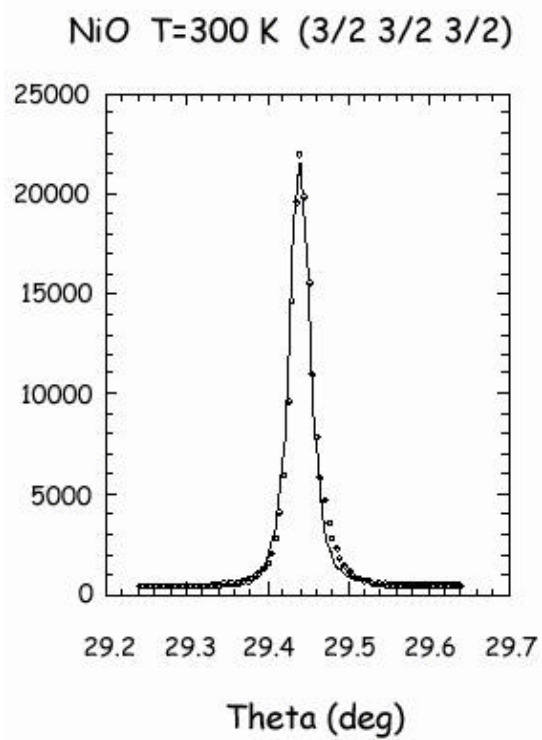


Additional magnetic reciprocal lattice vectors



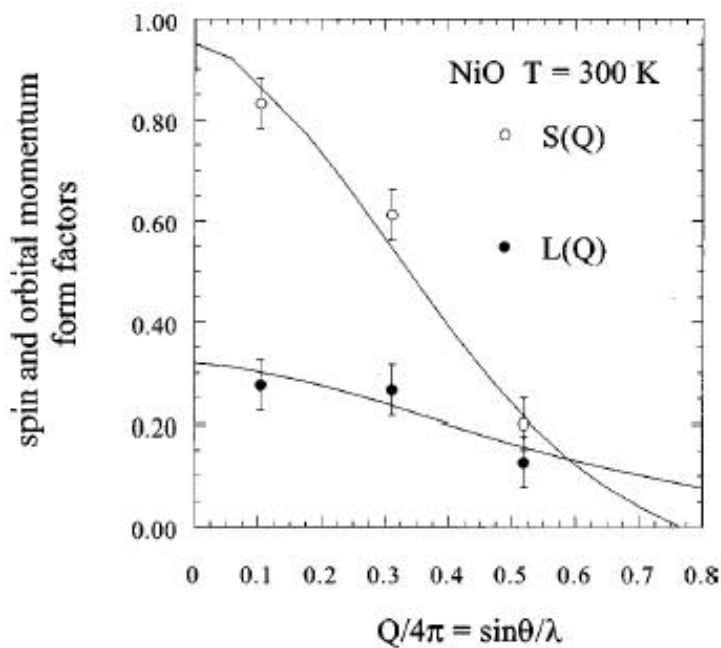
De Bergevin & Brunel, Phys. Lett. **A39**, 141 (1972)
Laboratory x-ray tube

NiO (3/2; 3/2; 3/2) reflection, counts /225 minutes



ESRF ID20 Beamline (counts/s)

V. Fernandez *et al.*, *Phys Rev.* **B57**, 7870 (1998)



V. Fernandez *et al.*,
Phys Rev. **B57**, 7870 (1998)

FIG. 6. Spin form factor and orbital-moment form factor in NiO. The data have been obtained by normalizing magnetic intensities to charge peaks corrected for extinction. Extrapolations at $K=0$ provide a value for the thermal average of $S=0.95\pm 0.10$ and $L=0.32\pm 0.05$ which lead to a value of $2.2\pm 0.3\mu_B$ for the staggered magnetization at $T=300$ K. The continuous lines are the calculated variations of $S(Q)$ and $L(Q)$ with $\sin\theta/\lambda$ from Refs. 18 and 24 with an expansion of the Q scale by 17%.

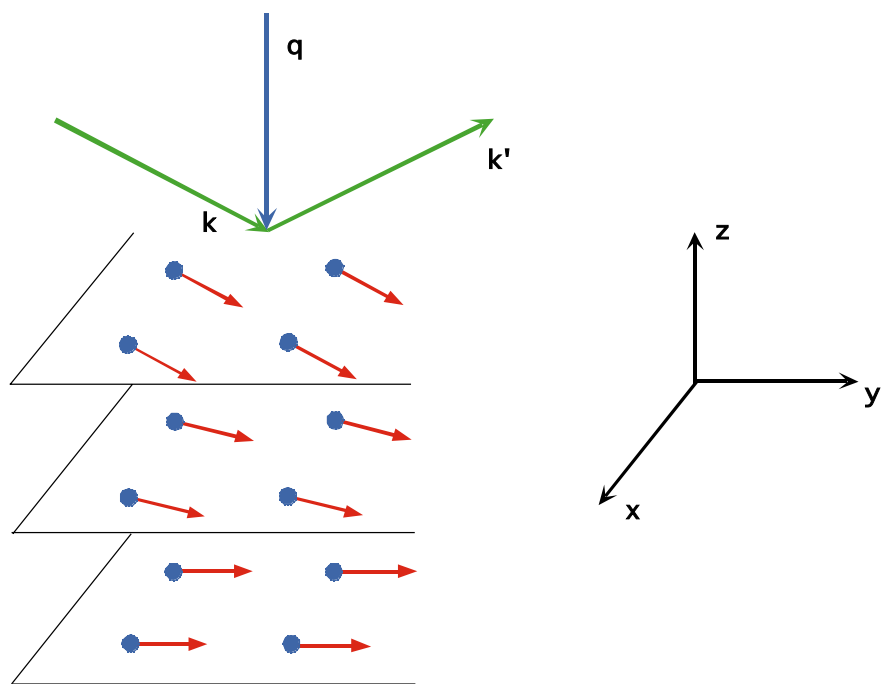


Fig. 6 Sketch of a basal-plane spiral antiferromagnet, and the scattering geometry

Arrangement of Moments in Holmium

Magnetic X-Ray Scattering Studies of Holmium Using Synchrotron Radiation

Doon Gibbs, D. E. Moncton, K. L. D'Amico, J. Bohr,^(a) and B. H. Grier^(b)
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973
 (Received 26 March 1985)

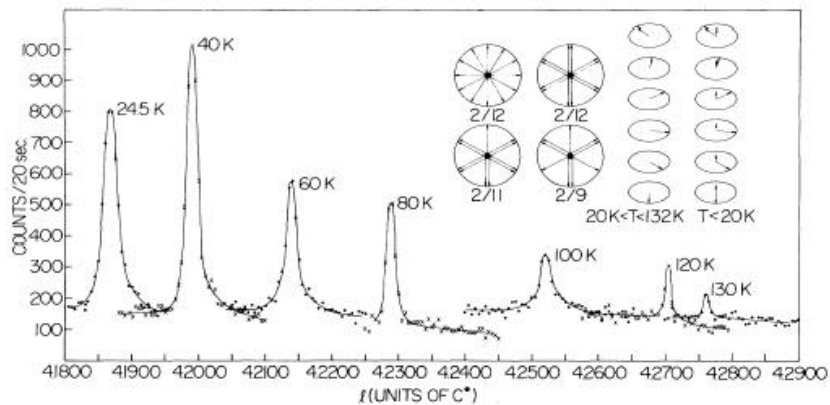
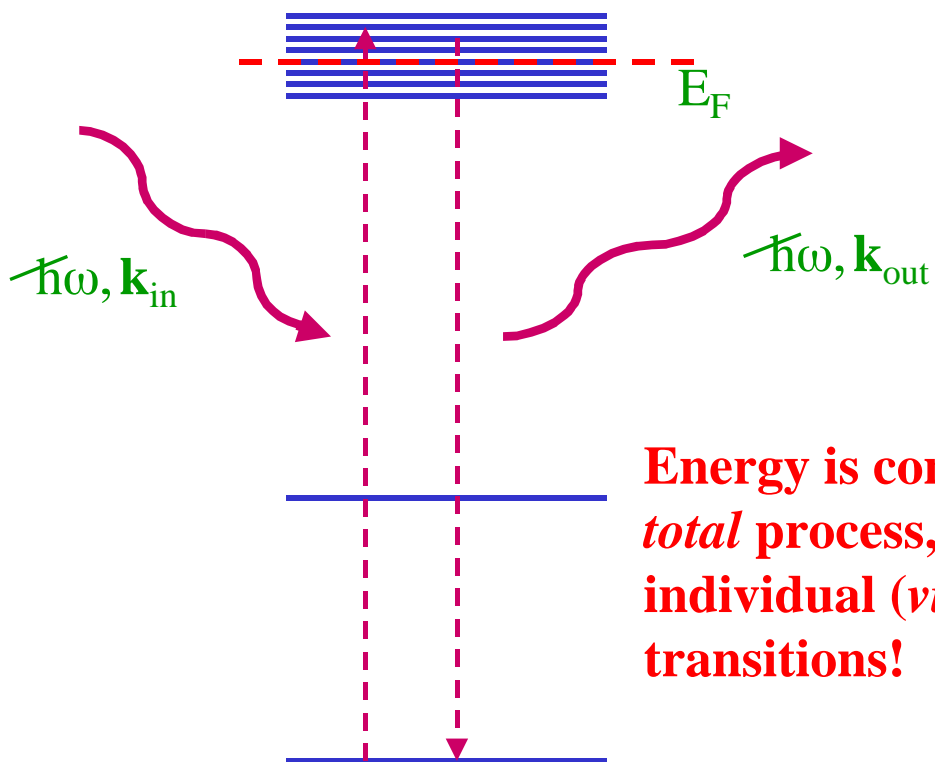


FIG. 1. Temperature dependence of the Ho(004)⁺ magnetic satellite taken with synchrotron radiation (lines drawn to guide the eye). Inset: Right, schematic representation of the magnetic structure of Ho (after Koehler⁹). Left, projections of the magnetic unit cell for different spin-slip structures. For simplicity the doublet has been drawn as two parallel spins.

Synchrotron X-rays have excellent angular resolution!

B Resonant (Anomalous) Scattering



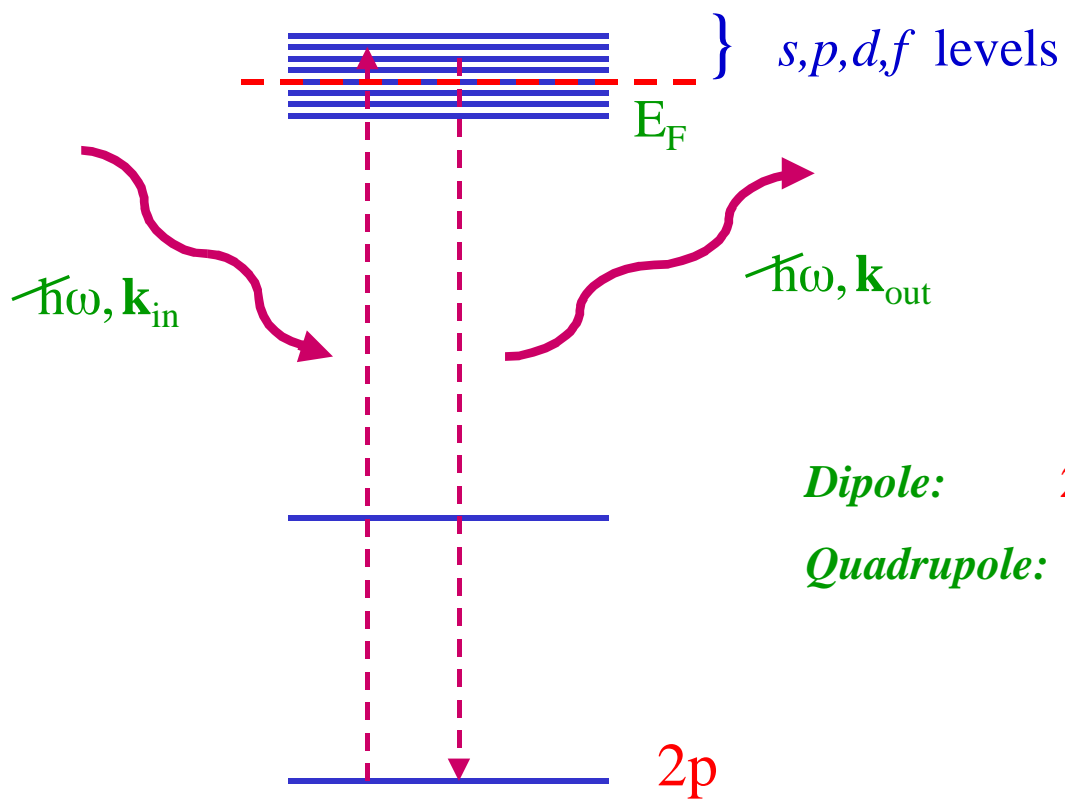
Energy is conserved in the total process, not in the individual (*virtual*) transitions!

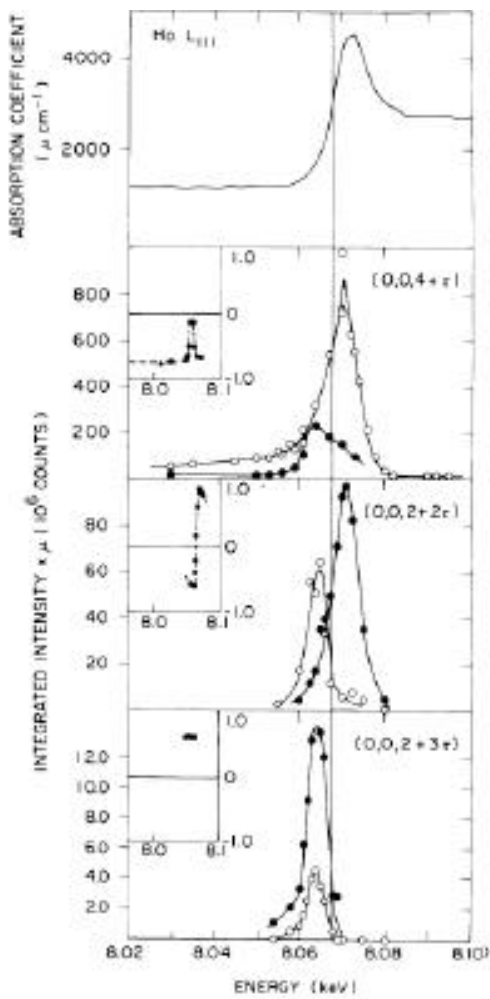
B Resonant scattering

Differential cross section $\rightarrow \frac{d\sigma}{d\Omega'} = |f_{res}|^2$ \leftarrow Scattering amplitude

$$f_{res} \cong \sum_n \frac{\langle 0 | \hat{\epsilon}^* \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | n \rangle \langle n | \hat{\epsilon}' \cdot \vec{p} e^{-i\vec{k}' \cdot \vec{r}} | 0 \rangle}{E_n - E_0 - \hbar\omega + i\Gamma_n / 2}$$

Multipole expansion: $e^{i\vec{k} \cdot \vec{r}} \cong 1 + i\vec{k} \cdot \vec{r} + \dots$





D. Gibbs et al.,
 Phys. Rev. Lett. **61**, 1241(1988)

Holmium, L_3 ($2p_{3/2}$ edge)

Polarization:

- **Parallel to scatt. Plane**
- **Perpendicular to scatt. plane**

B Resonant Magnetic Scattering

- 1. Is very intense (10^2 - 10^4 times more than non-resonant)**
- 2. Is element specific (via the core level binding energy)**
- 3. Its intensity is less directly related to magnetic moments**

Hannon-Trammel formula for dipole-dipole scattering

Definitions: $\vec{R} \equiv (X, Y, Z) = \sum_j \vec{r}_j$

$$R_0 = iZ, R_{\pm 1} = \mp(i/\sqrt{2})(X \pm iY)$$

\hat{z} Unit vector in z direction

$$f_{res} = -\frac{e^2}{mc^2} \left[\frac{1}{2} (\vec{e}'^*_{\lambda'} \cdot \vec{e}_{\lambda}) (F_{1,1}^{(e)} + F_{1,-1}^{(e)}) \right. \\ \left. - \frac{i}{2} (\vec{e}'^*_{\lambda'} \times \vec{e}_{\lambda}) \cdot \hat{z} (F_{1,1}^{(e)} - F_{1,-1}^{(e)}) \right. \\ \left. + (\vec{e}'^*_{\lambda'} \cdot \hat{z}) (\vec{e}_{\lambda} \cdot \hat{z}) (F_{1,0}^{(e)} - F_{1,1}^{(e)} - F_{1,-1}^{(e)}) \right]$$

Hannon *et al.*, Phys. Rev. Lett. 61, 1245 (1988)

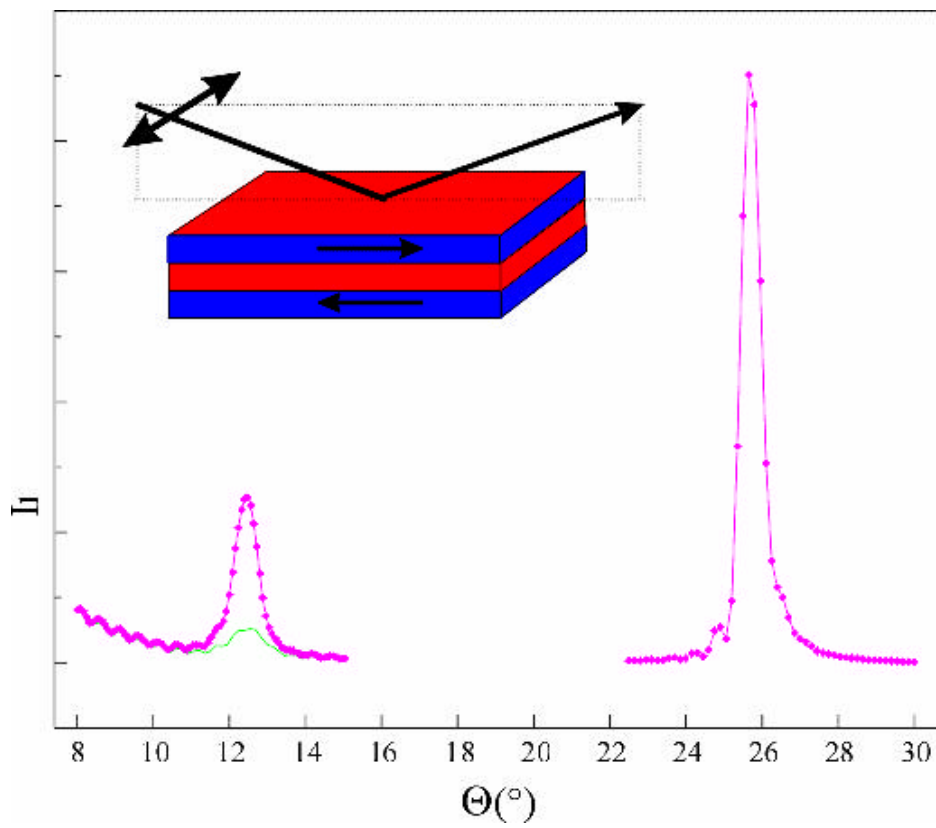
Soft X-ray Magnetic scattering:
structures with long periods.

Artificial structures (multilayers)

Complex compounds with large
structural and/or magnetic unit cells

$L_{2,3}$ edges of 3d transition metals

$2p \rightarrow 3d$



H Dürr *et al.*, $[\text{Co}(1 \text{ nm}) \text{Cu}(1 \text{ nm})]_{50}$ multilayer, Co L_3 -edge ($\sim 778 \text{ eV}$)

Soft X-Ray Resonant Magnetic Diffraction

S. B. Wilkins* and P. D. Hatton†

Department of Physics, University of Durham, Rochester Building, South Road, Durham DH1 3LE, United Kingdom

M. D. Roper

CLRC, Daresbury Laboratory, Warrington, Cheshire WA4 4AD, United Kingdom

D. Prabhakaran and A. T. Boothroyd

Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, United Kingdom

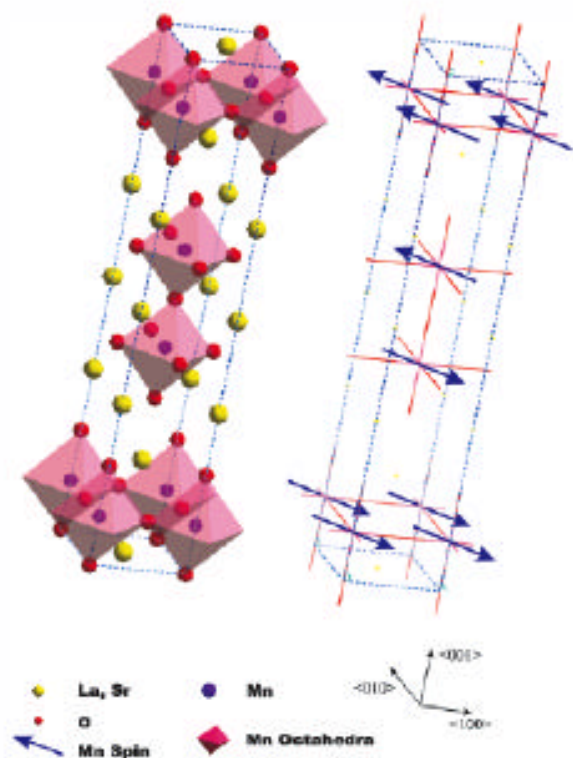
(Received 28 January 2003; published 8 May 2003)

We have conducted the first soft x-ray diffraction experiments from a bulk single crystal, studying the bilayer manganite $\text{La}_{1-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $x = 0.475$ in which we were able to access the (002) Bragg reflection using soft x rays. The Bragg reflection displays a strong resonant enhancement at the L_{III} and L_{II} manganese absorption edges. We demonstrate that the resonant enhancement of the magnetic diffraction of the (001) is extremely large, indeed so large that it exceeds that of the nonresonant Bragg diffraction. Resonant soft x-ray scattering of $3d$ transition metal oxides is the only technique for the atomic selective measurement of spin, charge, and orbital correlations in materials, such as high temperature superconductors, colossal magnetoresistance manganites, and charge stripe nickelates.

Spin ordering in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$

Two dimensional layered structure

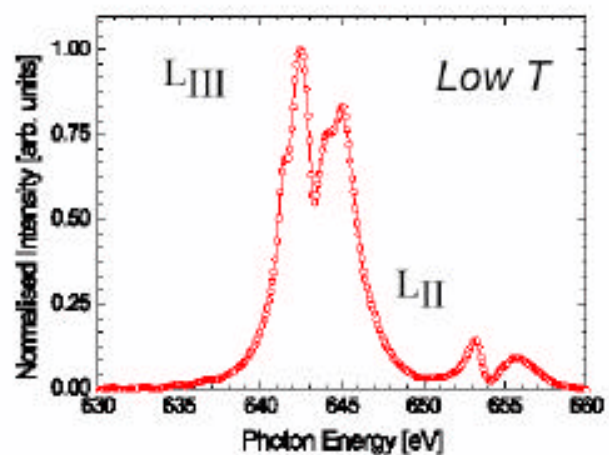
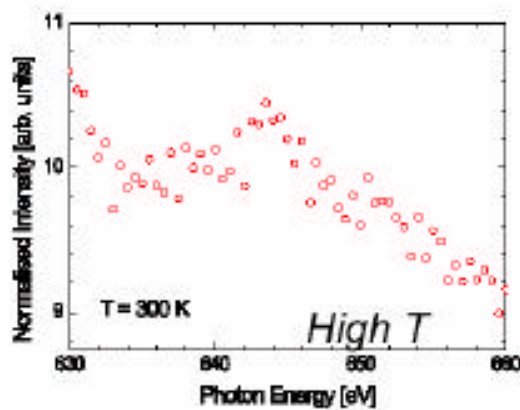
*At low temperatures
the Mn^{3+} and Mn^{4+}
ions spin order
antiferromagnetically*



Resonant magnetic exchange scattering

Below T_N the (001) is resonantly enhanced at the L_{III} and L_{II} edges

$2p \Rightarrow 3d$ transition



Above T_N only weak charge scatter is observed – no resonance. The (001) is due to AFM magnetic scattering.