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C. R. Physique 7 (2006) 262–266
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Physics/Solids, fluids: electronic and optical properties

Blending Bragg scattering with optical absorption: spectroscopy without a spectroscope

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Received 16 January 2006; accepted after revision 17 February 2006

Available online 31 March 2006

Presented by Philippe Nozières

Abstract

A double resonance method is proposed, blending resonant X-ray Bragg scattering with an optical laser that blurs the Bragg spots. One can detect the cross signal without resolving the satellite lines from the main beam, simply modulating the laser intensity at low frequency and carrying a synchronous detection. The concept is illustrated on two simple naive examples. ***To cite this article: Ph. Nozières, C. R. Physique 7 (2006).***

Résumé

Peut on marier la diffraction de Bragg et l'absorption optique : la spectroscopie sans spectroscope. Cette Note suggère une méthode de double résonance combinant la diffusion de Bragg résonnante d'un faisceau X de fréquence Ω avec l'absorption optique d'un faiceau laser de fréquence ω. Une détection synchrone permet d'observer le signal croisé sans résoudre les raies satellites de fréquence $(\Omega \pm \omega)$. Le concept est illustré sur deux exemples très simples. ***Pour citer cet article : Ph. Nozières, C. R. Physique 7 (2006).***

Keywords: Double resonance; Bragg scattering

Mots-clés : Double résonance ; Diffraction de Bragg

Usual *optical absorption* measures the average polarizability of a material. An a.c. electric field creates excitations with an electric dipole moment: it does not separate the contributions of different atoms within a unit cell. While irrelevant for simple materials, such a limitation becomes important when the unit cell contains many atoms. An alternate possibility is *X-ray Raman inelastic scattering*. Playing with the X-ray frequency Ω one can approach the resonance threshold of a deep level: the resulting *resonant scattering* is chemically sensitive (one can isolate the contribution of a given species). However, only hard X-rays penetrate a bulk sample—typically "K" spectra in the 10 keV range. Softer 'L' spectra are absorbed in a few hundreds Å: they are affected by the surface. Such K spectra face a resolution problem: isolating a 10 meV structure out of a 10 keV beam is a performance if the signal is strong;

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1631-0705/$ – see front matter
doi:10.1016/j.crhy.2006.02.011

it becomes hopeless if the signal is weak. Hence the interest of an experimental scheme that would avoid these resolution problems. We propose one such scheme in this Note, based on a double resonance set up. For simplicity we limit our discussion to single crystals, displaying coherent elastic Bragg scattering in which all lattice cells radiate in phase (they add their amplitudes instead of intensities). In addition to the X-ray beam with frequency Ω and amplitude A, we shine a laser with optical frequency ω and amplitude a, which creates the same excitations as in an absorption experiment. The novelty is to *observe these excitations through their effect on the Bragg spots*.

Let A be the incident X-ray amplitude, $A_{\rm sc}$ the elastically scattered amplitude. Laser irradiation modifies $A_{\rm sc}$ by a factor $[1 + \lambda|a|^2]$. The laser induced correction contains an elastic part at frequency Ω and satellites at frequency $(\Omega \pm \omega)$ *which we do not try to resolve*. We measure the *total* intensity: information on ω is provided by the laser, not by spectroscopy!

The effect is easily separated from the main beam in a *synchronous detection* scheme: we modulate the laser intensity $i = |a|^2 = i_0 + i_1 \cos \eta t$ at a low frequency η and we detect the in phase contribution in the scattered X-ray intensity. Such an approach has many advantages:

(i) the coherent Bragg scattering is intense;
(ii) both the laser and the X-ray can be made resonant: together with synchronous detection that should make the sensitivity high;
(iii) X-ray resonance is chemically selective;
(iv) comparing different Bragg vectors G differentiates atoms of the same species inside a lattice cell;
(v) X-ray and optical polarizations are additional degrees of freedom.

The method should be useful for complicated structures: we will illustrate it on a few simple examples. Let us emphasize that double resonance is in no way original: it goes back to the famous paper of Brossel and Bitter in 1952 [1]. Its many implementations show that it is much more than a plain addition of two tools. The present Note suggests yet another application in the field of X-rays.

1. Phonon excitations: a classical picture

The atom n in lattice cell i has position $(\mathbf{R}_i + \mathbf{r}_n)$. In an X-ray field with amplitude A it acquires a dipole moment $\mu_n(\Omega)$ proportional to A which radiates a scattered X-ray. Incident and scattered X-rays have wave vectors $\mathbf{Q}$ and $\mathbf{Q}'$. Bragg scattering corresponds to $\mathbf{Q}' - \mathbf{Q} = \mathbf{G}$, a Bragg vector of the reciprocal lattice such that $\exp(i\mathbf{G} \cdot \mathbf{R}_i) = 1$. The scattered X-ray amplitude is proportional to

$$A_f = \sum_n \mu_n(\Omega) \exp(i\mathbf{G} \cdot \mathbf{r}_n)$$

In order to shorten writing we define $\overline{\mu_n} = \mu_n \exp(i\mathbf{G} \cdot \mathbf{r}_n)$. If atoms are charged, the laser electric field displaces atoms by an amount $\mathbf{u}_n = \lambda_n a \cos \omega t$. The scattered amplitude becomes

$$A_f = \sum_n \overline{\mu_n} \exp(i\mathbf{G} \cdot \mathbf{u}_n) = \sum_n \overline{\mu_n} \left[1 + ia\mathbf{G} \cdot \lambda_n \cos \omega t - \frac{(\mathbf{G} \cdot \lambda_n)^2 a^2 \cos^2 \omega t}{2} \right]$$

The component at frequency Ω has amplitude

$$A_{f0} = \sum_n \overline{\mu_n} \left[1 - (\mathbf{G} \cdot \lambda_n)^2 a^2/4 \right]$$

hence an intensity

$$I_{f0} = \sum_{n,m} \overline{\mu_n}\,\overline{\mu_m} \left[1 - \frac{a^2}{4} \left[(\mathbf{G} \cdot \lambda_n)^2 + (\mathbf{G} \cdot \lambda_m)^2 \right] \right]$$

The satellites at frequency $(\Omega \pm \omega)$ have amplitude

$$A_{f1} = i \sum_n \overline{\mu_n} \mathbf{G} \cdot \lambda_n a/2$$

hence a global intensity

$$I_{f1} = |A_{f1}|^2 = \sum_{n,m} \left[\overline{\mu_n}\overline{\mu_m} \frac{a^2}{2} (\mathbf{G}\cdot\lambda_n)(\mathbf{G}\cdot\lambda_m) \right]$$

The satellites at frequency $(\Omega \pm 2\omega)$ have an intensity $\sim a^4$ which we ignore. The modes 0 and 1 have different wave vectors: they are incoherent when reaching the detector—we must therefore add intensities

$$I_f = I_{f0} + I_{f1} = \sum_{n,m} \overline{\mu_n}\overline{\mu_m} \left[1 - \frac{(Ga)^2}{4} (\mathbf{G}\cdot\lambda_n - \mathbf{G}\cdot\lambda_m)^2 \right]$$

Laser irradiation affects the total Bragg scattering even if we do not resolve the satellites from the central line! From then on we modulate the laser intensity at a low frequency η, $|a|^2 = i_0 + i_1 \cos \eta t$, and we use synchronous detection. The phonon spectrum is obtained scanning the laser frequency ω. We need a tunable laser in the infrared: one may try feasibility on an ionic crystal.

The issue is, of course, sensitivity. Let $\mathbf{E}$ be the electric field amplitude of the light beam. Its energy flux is $\phi = \varepsilon_0 E^2 c$ (c is the velocity of light). In the absence of damping, the induced ionic displacement $\mathbf{u}$ is

$$\mathbf{u} = \frac{e\mathbf{E}}{M(\omega_0^2 - \omega^2)}$$

where M is an average ionic mass. At resonance the amplitude is limited by damping, usually due to anharmonic decay. The latter is characterized by a quality factor Q,

$$\mathbf{u} = \frac{e\mathbf{E}Q}{M\omega_0^2}$$

For a flux $\phi = 1$ W/mm^2 we find $E = 200$ V/cm and for a light alkali atom $Gu \sim 2 \times 10^{-6} Q$. Even $Q = 100$ yields a very small 10^{-8} effect. Increasing a steady flux is precluded by heating: we must use pulsed laser irradiation in order to increase the electric field E significantly.

2. Electronic excitations: a 3 level toy system

A single atom has 3 states: a deep ground state 1 may be a $1s$ state in K X-ray spectroscopy. State 1 is excited into state 2 by an X-ray photon with frequency Ω, with a large amplitude close to resonance, $\Omega = E_2 - E_1$. State 2 is probed by an optical photon with frequency ω which excites it to state 3. If the two photons have the same polarization, state 2 may be a $2p$ state, state 3 a $2s$ state. The transition $2 \to 3$ is easily detected by direct spectroscopy: our issue is whether one can see it indirectly in the X-ray spectrum. Let A and a be the vector potentials of the two photons: the coupling matrix elements of the atom-photon system are

$$A \exp i\Omega t \, \langle 1|P|2\rangle = \bar{A}(t)$$
$$a \exp i\omega t \, \langle 2|P|3\rangle = \bar{a}(t)$$

where P is the momentum operator. The Hamiltonian is a 3×3 matrix

$$H = \begin{bmatrix} 0 & \bar{A} + \bar{a} & 0 \\ \bar{A}^* + \bar{a}^* & E_2 & \bar{A} + \bar{a} \\ 0 & \bar{A}^* + \bar{a}^* & E_3 \end{bmatrix}$$

where we have chosen E_1 as the origin of energies. We retain only those terms which are resonant

$$H = \begin{bmatrix} 0 & \bar{A} & 0 \\ \bar{A}^* & E_2 & \bar{a} \\ 0 & \bar{a}^* & E_3 \end{bmatrix}$$

We write the state vector as

$$|\Psi\rangle = \frac{1}{\sqrt{N}} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix}$$

where $N = \psi_1^2 + |\psi_2|^2 + |\psi_3|^2$. $|\Psi\rangle$ obeys the time dependent Schrödinger equation

$$i\frac{d\psi_1}{dt} = \bar{A}\psi_2$$
$$i\frac{d\psi_2}{dt} = E_2\psi_2 + \bar{A}^*\psi_1 + \bar{a}\psi_3$$
$$i\frac{d\psi_3}{dt} = E_3\psi_3 + \bar{a}^*\psi_2$$

In zeroth order $\psi_1 = 1$, $\psi_2 = \psi_3 = 0$. In first order $\psi_2 = -\bar{A}^*/(E_2 - \Omega) \sim \exp(-i\Omega t)$. In second order

$$\psi_3 = \frac{\bar{A}^*\bar{a}^*}{(E_2 - \Omega)(E_3 - \Omega - \omega)} \sim \exp\bigl[-i(\Omega + \omega)t\bigr]$$

(A correction of order A^*A to ψ_1 is ignored since we treat the X-ray amplitude in a linear approximation—in the same spirit we drop normalization corrections $\sim|\bar{A}|^2$.) In third order ψ_3 reacts on ψ_2 which becomes

$$\psi_2 = -\frac{\bar{A}^*}{(E_2 - \Omega)}\left[1 - \frac{\bar{a}^*\bar{a}}{(E_3 - \Omega - \omega)\ (E_2 - \Omega)}\right] \sim \exp(-i\Omega t)$$

The amplitude of state 2 is reduced by laser pumping to state 3.

The a.c. dipole moment responsible for X-ray scattering is proportional to

$$\langle\psi_1|P|\psi_2\rangle + \langle\psi_2|P|\psi_3\rangle$$

The elastically scattered X-ray amplitude comes from the first term

$$\frac{A_{\rm sc}}{A} \sim 1 - \frac{\bar{a}^*\bar{a}}{(E_3 - \Omega - \omega)(E_2 - \Omega)}$$

The correction is again proportional to the *intensity* $|a|^2$ of the low frequency beam. Because it adds to 1, the effect on the X-ray intensity is twice as big. Once again it can be detected by a low frequency modulation of the ω beam together with synchronous detection.

In both experiments the X-ray scattering remains perfectly elastic: one retains the coherent nature of Bragg scattering. In contrast to the preceding example there is no satellite at $(\Omega \pm \omega)$ because of reflection symmetry, which precludes mixing of an odd number of photon operators. The smallness of non linear phenomena should be compensated by the resonant nature of scattering $1 \to 2$ as well as by the Bragg geometry that adds amplitudes instead of intensities.

3. Improving synchronous detection?

Standard synchronous detection applies to analogic continuous signals: it works equally well when counting discrete events. If individual photons arrive at time t_p, instead of adding 1 at each arrival we ask a computer to add $\exp i\eta t_p$ where η is the low frequency modulation of the laser intensity. After n photons, the measured quantity is

$$\lambda_n = \sum_{p=1}^{n} \exp i\eta t_p$$

Let the steady flux be ϕ_0, the modulated flux $\phi_1 = \varepsilon\phi_0$. If ϕ_0 has no noise it is eliminated after a time $t^* \sim 1/\varepsilon\eta$: for a megacycle modulation that is quite reasonable. The issue is thus the *noise of the incoming beam*. The shot noise due to the discrete nature of photons seems to be negligible for the very high X-ray flux under consideration: we may consider the photon flux per second as a continuous function of time $\phi(t)$, itself sum of an average ϕ_0 and a noise $\delta\phi$ characterized by its spectrum

$$\overline{\delta\phi^*(\omega)\delta\phi(\omega')} = G(\omega)\delta(\omega - \omega')$$

Let us mimic the duration t^* of the experiment by an exponential cut off $\gamma \sim 1/t^*$. The measured quantity is

$$\int_0^\infty dt'\,\phi(t')\exp(-i\eta t' - \gamma t') = \frac{\phi_0}{\gamma} + \int d\omega \frac{\delta\phi(\omega)}{i(\omega - \eta) + \gamma}$$

The mean square amplitude of the noise term is

$$\int d\omega\, d\omega' \frac{\delta\phi(\omega)\delta\phi(\omega')^*}{(i(\omega-\eta)+\gamma)(-i(\omega'-\eta)+\gamma)} = \frac{2\pi}{\gamma} G(\eta)$$

As expected what matters is the noise of the incoming beam at the modulation frequency η, which is hard to estimate. The noise induced signal grows as $\sqrt{G(\eta)t}$ while the wanted modulation is $\phi_1 = \varepsilon\phi_0 t$ where ε is very small. Sorting the signal out of noise takes a time

$$t^* \sim \frac{G(\eta)}{(\varepsilon\phi_0)^2}$$

t^* grows as $1/\varepsilon^2$ which becomes murderous. A way out is to scale the 'signal' $\exp i\omega t_p$ by the incoming flux $\phi_0(t_p)$ which must be measured independently. A pulse set up is well adapted to that correction: a '+' pulse has a constant laser intensity, a '−' pulse has no laser. One may conceive two samples in line, one (a) with no laser which monitors the flux, one (b) with the laser modulation on. One counts a large number N of events on beam (a) during which beam (b) registers $+1$, then the *same number* of events on beam (a) during the other half cycle, during which beam (b) registers -1. Sample (a) acts as a *clock* which locks the pulse to a fixed number of events. The two samples need not be identical: the clock only guarantees that $+$ and $-$ pulses have identical length. That should automatically eliminate fluctuations of the incoming flux, thereby returning to the comfortable $t^* \sim 1/\varepsilon\eta$. Whether that is a theorist's dream remains to be seen!

4. Conclusion

It appears possible to detect optical absorption indirectly as a modification of resonant X-ray Bragg scattering. In this way one can exploit the chemical selectivity of X-ray resonances, as well as the geometric information inside a lattice cell provided by the various Bragg vectors G. Additional information is provided by the polarizations of both X-rays and laser fields. Such a flexible approach should prove a powerful tool for complicated materials, containing many atoms inside a unit cell. It is possible in practice because one does not need to resolve the frequency transfer ω out of the primary X-ray beam Ω. The external laser fixes ω and a plain low frequency modulation of its intensity allows a synchronous detection of the modulation: the large gain in sensitivity is promising.

One can extend the 3 level model to a more realistic situation, in which a local core state is coupled to a whole valence band. Such an experiment measures a four point correlation function (the generalization of the satellites of Section 2). The calculation is less transparent: it will be published elsewhere.

References

[1] J. Brossel, F. Bitter, Phys. Rev. 86 (1952) 308.