

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

The chirality of type-II reflections can be used to distinguish enantiomorphous crystals. Although this was suggested many years ago, its potential was only recently proved by experiments, first on α -quartz, SiO_2 , and berlinite, AlPO_4 (Tanaka *et al.*, 2008; Tanaka, Kojima *et al.*, 2010), later for tellurium (Tanaka, Collins *et al.*, 2010). All three candidates crystallize in the space groups $P3_121$ or $P3_221$. The case of tellurium is particularly interesting because standard X-ray diffraction methods for absolute structure determination fail in elemental crystals.

The non-trivial polarization and azimuthal properties discussed above are, in most cases, determined by symmetry, and they are used as evidence confirming the origin of the forbidden reflections. They are also used for obtaining detailed information about anisotropy of local susceptibility and, hence, about structural and electronic properties. For instance, careful analysis of polarization and azimuthal dependences allows one to distinguish between different scenarios of the Verwey phase transition in magnetite, Fe_3O_4 – a longstanding and confusing problem (see Hagiwara *et al.*, 1999; García *et al.*, 2000; Renevier *et al.*, 2001; García & Subías, 2004; Nazarenko *et al.*, 2006; Subías *et al.*, 2012).

1.11.4. Physical mechanisms for the anisotropy of atomic X-ray susceptibility

Conventional non-resonant Thomson scattering in condensed matter is the result of the interaction of the electric field of the electromagnetic wave with the charged electron subsystem. However, there are also other mechanisms of interaction, *e.g.* interaction of electromagnetic waves with spin and orbital moments, which was first considered by Platzman & Tzoar (1970) for molecules and solids. They predicted the sensitivity of X-ray diffraction to a magnetic structure of a crystal, as later observed in the pioneering works of de Bergevin & Brunel (de Bergevin & Brunel, 1972, 1981; Brunel & de Bergevin, 1981). It is reasonable to describe all X-ray–electron interactions by the Pauli equation (Berestetskii *et al.*, 1982), which is a low-energy approximation to the Dirac equation (typical X-ray energies are $\hbar\omega \ll mc^2 \approx 0.5$ MeV where m is the electron mass). The equation accounts for charge and spin interaction with the electromagnetic field of the wave, and spin–orbit interaction (Blume, 1985, 1994) using the following Hamiltonian:

$$\begin{aligned}
 H' = & \frac{e^2}{2mc^2} \sum_p \mathbf{A}^2(\mathbf{r}_p) - \frac{e}{mc} \sum_p \mathbf{P}_p \cdot \mathbf{A}(\mathbf{r}_p) \\
 & - \frac{e\hbar}{mc} \sum_p \mathbf{s}_p \cdot [\nabla \times \mathbf{A}(\mathbf{r}_p)] \\
 & - \frac{e^2\hbar}{2(mc^2)^2} \sum_p \mathbf{s}_p \cdot [\dot{\mathbf{A}}(\mathbf{r}_p) \times \mathbf{A}(\mathbf{r}_p)], \quad (1.11.4.1)
 \end{aligned}$$

where \mathbf{P}_p is the momentum of the p th electron, and $\mathbf{A}(\mathbf{r}_p)$ is the vector potential of the electromagnetic wave with wavevector \mathbf{k} and polarization \mathbf{e} .

Here and below $\mathbf{A} = \sum_{\mathbf{k}, \alpha} (2\pi\hbar c^2/V\omega_{\mathbf{k}})^{1/2} [\mathbf{e}(\mathbf{k}\alpha)c(\mathbf{k}\alpha)\exp(i\mathbf{k}\cdot\mathbf{r}) + \mathbf{e}^*(\mathbf{k}\alpha)c^+(\mathbf{k}\alpha)\exp(-i\mathbf{k}\cdot\mathbf{r})]$, where V is a quantization volume, index α labels two polarizations of each wave, $\mathbf{e}(\mathbf{k}\alpha)$ are the polarizations vectors, and $c(\mathbf{k}\alpha)$ and $c^+(\mathbf{k}\alpha)$ are the photon annihilation and creation operators.

Considering X-ray scattering by different atoms in solids as independent processes [in Section 1.2.4 of *International Tables for Crystallography* Volume B, this is called ‘the isolated-atom

approximation in X-ray diffraction’; the validity of this approximation has been discussed by Kolpakov *et al.* (1978)], the atomic scattering amplitude f , which describes the scattering of a wave with wavevector \mathbf{k} and polarization \mathbf{e} into a wave with wavevector \mathbf{k}' and polarization \mathbf{e}' , can be written as

$$f(\mathbf{k}, \mathbf{e}, \mathbf{k}', \mathbf{e}') = -\frac{e^2}{mc^2} f_{jk}(\mathbf{k}', \mathbf{k}) e_j'^* e_k, \quad (1.11.4.2)$$

where the tensor atomic factor $f_{jk}(\mathbf{k}', \mathbf{k})$ depends not only on the wavevectors but also on the atomic environment, magnetic and orbital moments *etc.* From equation (1.11.4.1) and with the help of perturbation theory (Berestetskii *et al.*, 1982), the atomic factor $f_{jk}(\mathbf{k}', \mathbf{k})$ can be expressed as

$$\begin{aligned}
 f_{jk}(\mathbf{k}', \mathbf{k}) = & \sum_a p_a \left\{ \langle a | \sum_p \exp(i\mathbf{G} \cdot \mathbf{r}_p) | a \rangle \delta_{jk} \right. \\
 & - i \frac{\hbar\omega}{mc^2} \langle a | \sum_p \exp(i\mathbf{G} \cdot \mathbf{r}_p) \left(-i \frac{[\mathbf{G} \times \mathbf{P}_p]_l}{\hbar H^2} A_{jkl} + s_l^p B_{jkl} \right) | a \rangle \\
 & - \frac{1}{m} \sum_c \left(\frac{E_a - E_c}{\hbar\omega} \right) \frac{\langle a | O_j^+(\mathbf{k}') | c \rangle \langle c | O_k(\mathbf{k}) | a \rangle}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} \\
 & \left. + \frac{1}{m} \sum_c \left(\frac{E_a - E_c}{\hbar\omega} \right) \frac{\langle a | O_k(\mathbf{k}) | c \rangle \langle c | O_j^+(\mathbf{k}') | a \rangle}{E_a - E_c - \hbar\omega} \right\}, \quad (1.11.4.3)
 \end{aligned}$$

where the first line describes the non-resonant Thomson scattering and Γ is the energy width of the excited state $|c\rangle$. The second line gives non-resonant magnetic scattering with the spin and orbital terms given by the rank-3 tensors B_{jkl} (1.11.5.2) and A_{jkl} (1.11.5.1), respectively. Compared to the second-to-last line, where the energy denominator can be close to zero, the last line is usually neglected, but sometimes it has to be added to the non-resonant terms, in particular at photon energies far from resonance. The third term gives the dispersion corrections also addressed as resonant scattering, magnetic and non-magnetic. In equation (1.11.4.3), E_a and E_c are the ground and excited states energies, respectively; p_a is the probability that the incident state of the scatterer $|a\rangle$ is occupied; and $\mathbf{G} = \mathbf{k} - \mathbf{k}'$ is the scattering vector (in the case of diffraction $|\mathbf{G}| = 4\pi \sin \theta/\lambda$, where θ is the Bragg angle). The vector operator $\mathbf{O}(\mathbf{k})$ has the form

$$\mathbf{O}(\mathbf{k}) = \sum_p \exp(i\mathbf{k} \cdot \mathbf{r}_p) (\mathbf{P}_p - i\hbar[\mathbf{k} \times \mathbf{s}_p]). \quad (1.11.4.4)$$

The second term in this equation is small and is frequently omitted.

In general, the total atomic scattering factor looks like

$$\begin{aligned}
 f_{jk}(\mathbf{k}', \mathbf{k}, E) = & [f_0(|\mathbf{k}' - \mathbf{k}|) + f_0'(E) + if_0''(E)] \delta_{ij} \\
 & + f_{jk}'(\mathbf{k}', \mathbf{k}, E) + if_{jk}''(\mathbf{k}', \mathbf{k}, E) + f_{jk}^{\text{mag}}, \quad (1.11.4.5)
 \end{aligned}$$

where f_0 is the ordinary Thomson (non-resonant) factor, $f_0'(E)$ and $f_0''(E)$ are the isotropic corrections to the dispersion and absorption, which become stronger near absorption edges ($\sim 10^{-1}f_0$), and $f_{ij}'(\mathbf{k}', \mathbf{k}, E)$ and $f_{ij}''(\mathbf{k}', \mathbf{k}, E)$ are the real and imaginary contributions accounting for resonant anisotropic scattering and are sensitive to the local symmetry of the resonant atom and its magnetism. In the latter case, one should add the tensor f_{ij}^{mag} ($\sim 10^{-2}$ – $10^{-3}f_0$) describing magnetic non-resonant scattering, which is also anisotropic (see the next section).