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In order to separate these contributions, we write formally $\chi(\mathbf{E}) = \chi(\mathbf{E}, Q_p(\mathbf{E}), \mathbf{S}(\mathbf{E}))$ and get, to first order in the field,

$$\begin{aligned}\delta\chi(\mathbf{E}) &= (\partial\chi/\partial\mathbf{E})\mathbf{E} + \sum_p(\partial\chi/\partial Q_p)Q_p(\mathbf{E}) + (\partial\chi/\partial\mathbf{S})\mathbf{S}(\mathbf{E})\\ &= \sum_j \mathbf{R}^{jE}\mathbf{E}Q_j, \text{ where we define}\\ \mathbf{R}^{jE} &= (\partial\mathbf{R}^j/\partial\mathbf{E}) + \sum_p(\partial\mathbf{R}^j/\partial Q_p)(\mathrm{d}Q_p/\mathrm{d}\mathbf{E}) + (\partial\mathbf{R}^j/\partial\mathbf{S})\mathbf{d}.\end{aligned} \tag{2.3.4.4}$$

The first term in these equations involves the susceptibility derivative $\mathbf{b} = (\partial\chi/\partial\mathbf{E})$ at constant Q_p and $\mathbf{S}$. The second term involves the second-order susceptibility derivatives with respect to the normal coordinates: $\chi^{(j,p)} = (\partial^2\chi/\partial Q_j\partial Q_p) = (\partial R^j_{\alpha\beta}/\partial Q_p)$. Since $Q_p(\mathbf{E}) \sim Z_{p\nu}E_\nu$, where the quantity $\mathbf{Z}_p = (Z_{p\nu})$ is the effective charge tensor (2.3.3.4) of the normal mode p, its nonzero contributions are possible only if there are infrared-active optical phonons (for which, in principle, $\mathbf{Z}_p \neq 0$) in the crystal. The third term is proportional to the field-induced elastic strain $\mathbf{S}(\mathbf{E}) = \mathbf{dE}$ *via* the elasto-optic tensor $\mathbf{p} = (\partial\chi/\partial\mathbf{S})$ and can occur only in piezoelectric crystals.

Example: As an illustration, we derive the matrix form of linear electric-field-induced Raman tensors (including possible antisymmetric part) in a tetragonal crystal of the $4mm$ class. The corresponding representation $[\Gamma_{\rm PV}\otimes\Gamma_{\rm PV}]\otimes\Gamma_{\rm PV}$ in this class reduces as follows:

$$[\Gamma_{\rm PV}\otimes\Gamma_{\rm PV}]_S\otimes\Gamma_{\rm PV} = 3\mathrm{A}_1\oplus\mathrm{A}_2\oplus 2\mathrm{B}_1\oplus 2\mathrm{B}_2\oplus 5\mathrm{E},$$
$$[\Gamma_{\rm PV}\otimes\Gamma_{\rm PV}]_A\otimes\Gamma_{\rm PV} = \mathrm{A}_1\oplus 2\mathrm{A}_2\oplus\mathrm{B}_1\oplus\mathrm{B}_2\oplus 2\mathrm{E}.$$

Suitable sets of symmetrized (s) and antisymmetrized (a) basis functions (third-order polynomials) for the representations of the $4mm$ point group can be easily derived by inspection or using projection operators. The results are given in Table 2.3.4.1. Using these basis functions, one can readily construct the Cartesian form of the linear contributions to the electric-field-induced Raman tensors $\mathbf{R}^j(\mathbf{E}) = \mathbf{R}^{jE}\mathbf{E}$ for all symmetry species of the $4mm$-class crystals. The tensors are split into symmetric (conventional allowed scattering) and antisymmetric part.

Symmetric / Antisymmetric

$$\mathrm{A}_1: \begin{pmatrix} a_1E_z & . & a_2E_x\\ . & a_1E_z & a_2E_y\\ a_2E_x & a_2E_y & b_1E_z\end{pmatrix} + \begin{pmatrix} . & . & a_3E_x\\ . & . & a_3E_y\\ -a_3E_x & -a_3E_y & .\end{pmatrix}$$

$$\mathrm{A}_2: \begin{pmatrix} . & . & c_2E_y\\ . & . & -c_2E_x\\ c_2E_y & -c_2E_x & .\end{pmatrix} + \begin{pmatrix} . & c_1E_z & c_3E_y\\ -c_1E_z & . & -c_3E_x\\ -c_3E_y & c_3E_x & .\end{pmatrix}$$

$$\mathrm{B}_1: \begin{pmatrix} d_1E_z & . & d_2E_x\\ . & -d_1E_z & -d_2E_y\\ d_2E_x & -d_2E_y & .\end{pmatrix} + \begin{pmatrix} . & . & d_3E_x\\ . & . & -d_3E_y\\ -d_3E_x & d_3E_y & .\end{pmatrix}$$

$$\mathrm{B}_2: \begin{pmatrix} . & e_1E_z & e_2E_y\\ e_1E_z & . & e_2E_x\\ e_2E_y & e_2E_x & .\end{pmatrix} + \begin{pmatrix} . & . & e_3E_y\\ . & . & e_3E_x\\ -e_3E_y & -e_3E_x & .\end{pmatrix}$$

$$\mathrm{E}: \begin{pmatrix} (f_1+f_2)E_x & f_4E_y & f_5E_z\\ f_4E_y & (f_1-f_2)E_x & .\\ f_5E_z & . & f_3E_x\end{pmatrix} + \begin{pmatrix} . & g_4E_y & g_5E_z\\ -g_4E_y & . & .\\ -g_5E_z & . & .\end{pmatrix}$$

$$\begin{pmatrix} (f_1-f_2)E_y & f_4E_x & .\\ f_4E_x & (f_1+f_2)E_y & f_5E_z\\ . & f_5E_z & f_3E_y\end{pmatrix} + \begin{pmatrix} . & -g_4E_x & .\\ g_4E_x & . & g_5E_z\\ . & -g_5E_z & .\end{pmatrix}$$

2.3.4.3. *Raman scattering in a magnetic field*

In a magnetic field, the dielectric susceptibility tensor of a crystal is known to obey the general relation (Onsager reciprocity theorem for generalized kinetic coefficients)

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\beta\alpha}(-\mathbf{H}). \tag{2.3.4.5}$$

Further, in the absence of absorption, the susceptibility must be Hermitian, *i.e.*

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi^*_{\beta\alpha}(\mathbf{H}). \tag{2.3.4.6}$$

Hence, $\boldsymbol{\chi}(\mathbf{H})$ is neither symmetric nor real. Expanding $\boldsymbol{\chi}(\mathbf{H})$ in the powers of the field,

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\alpha\beta}(0) + \frac{\partial\chi_{\alpha\beta}}{\partial H_\mu}H_\mu + \frac{\partial^2\chi_{\alpha\beta}}{\partial H_\mu\partial H_\nu}H_\mu H_\nu + \ldots, \tag{2.3.4.7}$$

it follows that all terms of the magnetic-field-induced Raman tensor that are of odd powers in $\mathbf{H}$ are purely imaginary and antisymmetric in α and β, whereas all terms of even powers in $\mathbf{H}$ are real and symmetric.

Let us discuss in more detail the symmetry properties of the first-order term, which can be written as

$$\Delta\chi_{\alpha\beta}(\mathbf{H}) = if_{\alpha\beta\mu}H_\mu, \tag{2.3.4.8}$$

where the tensor $\mathbf{f}$, referred to as the *magneto-optic tensor*, is real and purely antisymmetric in the first two indices:

$$f_{\alpha\beta\nu} \equiv -i(\partial\chi_{\alpha\beta}/\partial H_\nu) = -f_{\beta\alpha\nu}.$$

The representation $\Gamma(\mathbf{f})$ of the magneto-optic tensor $\mathbf{f}$ may thus be symbolically written as

$$\begin{aligned}\Gamma(\mathbf{f}) &= [\Gamma_{\rm PV}\otimes\Gamma_{\rm PV}]_A\otimes\Gamma_{\rm AV} = \Gamma_{\rm AV}\otimes\Gamma_{\rm AV} = \Gamma_{\rm PV}\otimes\Gamma_{\rm PV}\\ &= \Gamma(T_\alpha T_\beta),\end{aligned} \tag{2.3.4.9}$$

since the antisymmetric part of the product of two polar vectors transforms like an axial vector, and the product of two axial vectors transforms exactly like the product of two polar vectors. Hence, the representation $\Gamma(\mathbf{f})$ is equivalent to the representation of a general nonsymmetric second-rank tensor and reduces in exactly the same way (2.3.3.14).

$$\Gamma(\mathbf{f}) = \Gamma_{\rm PV}\otimes\Gamma_{\rm PV} = c^{(1)}\Gamma(1)\oplus c^{(2)}\Gamma(2)\oplus\ldots.$$

We arrive thus at the important conclusion that, to first order in the field, only the modes that normally show intrinsic Raman activity (either symmetric and antisymmetric) can take part in magnetic-field-induced scattering. Moreover, the magnetic-field-induced Raman tensors for these symmetry species must have the same number of components as the general nonsymmetric Raman tensors at zero field.

In order to determine the symmetry-restricted matrix form of the corresponding field-induced Raman tensors (linear in $\mathbf{H}$) in Cartesian coordinates, one can use the general method and construct the tensors from the respective (antisymmetric) basis functions. In this case, however, a simpler method can be adopted, which makes use of the transformation properties of the magneto-optic tensor as follows.

From the definition of the tensor $\mathbf{f}$, it is clear that its Cartesian components $f_{\alpha\beta\nu}$ must have the same symmetry properties as the product $[E_\alpha E_\beta]_A H_\nu$. The antisymmetric factor $[E_\alpha E_\beta]_A$ transforms, however, as $\varepsilon_{\alpha\beta\mu}H_\mu$, where $\varepsilon_{\alpha\beta\mu}$ is the fully antisymmetric third-rank pseudotensor (*Levi–Civita tensor*). Consequently, $f_{\alpha\beta\nu}$ must transform in the same way as $\varepsilon_{\alpha\beta\mu}H_\mu H_\nu$, which in turn transforms identically to $\varepsilon_{\alpha\beta\mu}E_\mu E_\nu$. Therefore, comparison of the matrices corresponding to the irreducible components $\Gamma(j)$ provides a simple mapping between the components of the Cartesian forms of the linear field-induced Raman tensors $\mathbf{R}^j(\mathbf{H}) = \mathbf{R}^{jh}\mathbf{H}$ and the intrinsic Raman tensors $\mathbf{R}^{j0}$. Explicitly, this mapping is given by

$$R^{jH}_{\alpha\beta\nu} \equiv \frac{\partial^2\chi_{\alpha\beta}}{\partial Q_j\partial H_\nu} = if^{(j)}_{\alpha\beta\nu} \;\leftarrow\; i\varepsilon_{\alpha\beta\mu}R^{jo}_{\mu\nu}. \tag{2.3.4.10}$$

For any given symmetry species, this relation can be used to deduce the matrix form of the first-order field-induced Raman tensors from the tensors given in Table 2.3.3.1.

Example: We consider again the $4mm$ class crystal. The representation $\Gamma(\mathbf{f})$ of the magneto-optic tensor $\mathbf{f}$ in the $4mm$ class reduces as follows:

$$\Gamma(\mathbf{f}) = \Gamma_{\rm PV} \otimes \Gamma_{\rm PV} = 2{\rm A}_1 \oplus {\rm A}_2 \oplus {\rm B}_1 \oplus {\rm B}_2 \oplus 2{\rm E}.$$

Straightforward application of the mapping mentioned above then gives the following symmetry-restricted matrix forms of contributions to the magnetic-field-induced Raman tensors $\mathbf{R}^{jH}\mathbf{H}$ for all symmetry species of the $4mm$-class crystals. The number of independent parameters for each species is the same as in the intrinsic nonsymmetric zero-field Raman tensors:

$$A_1: \begin{pmatrix} . & ib'H_z & -ia'H_y \\ -ib'H_z & . & ia'H_x \\ ia'H_y & -ia'H_x & . \end{pmatrix}$$

$$A_2: \begin{pmatrix} . & . & ic'H_x \\ . & . & ic'H_y \\ -ic'H_x & -ic'H_y & . \end{pmatrix}$$

$$B_1: \begin{pmatrix} . & . & id'H_y \\ . & . & id'H_x \\ -id'H_y & -id'H_x & . \end{pmatrix}$$

$$B_2: \begin{pmatrix} . & . & -ie'H_x \\ . & . & ie'H_y \\ ie'H_x & -ieH_y & . \end{pmatrix}$$

$$E: \begin{pmatrix} . & ig'H_x & . \\ -ig'H_x & . & if'H_z \\ . & -if'H_z & . \end{pmatrix} \begin{pmatrix} . & ig'H_y & -if'H_z \\ -ig'H_y & . & . \\ if'H_z & . & . \end{pmatrix}.$$

Let us note that the conclusions mentioned above apply, strictly speaking, to non-magnetic crystals. In magnetic materials in the presence of spontaneous ordering (*ferro-* or *antiferromagnetic* crystals) the analysis has to be based on magnetic point groups.

2.3.4.4. *Stress- (strain-) induced Raman scattering*

Stress-induced Raman scattering is an example of the case when the external 'force' is a higher-rank tensor. In the case of stress, we deal with a symmetric second-rank tensor. Since symmetric stress ($\mathbf{T}$) and strain ($\mathbf{S}$) tensors have the same symmetry and are uniquely related *via* the fourth-rank *elastic stiffness tensor* ($\mathbf{c}$),

$$T_{\alpha\beta} = c_{\alpha\beta\mu\nu}S_{\mu\nu},$$

it is immaterial for symmetry purposes whether stress- or strain-induced effects are considered. The linear strain-induced contribution to the susceptibility can be written as

$$\Delta\chi_{\alpha\beta}(\mathbf{S}) = \left(\frac{\partial\chi_{\alpha\beta}}{\partial S_{\mu\nu}}\right)S_{\mu\nu}$$

so that the respective strain coefficients (conventional symmetric scattering) transform evidently as

$$[\Gamma_{\rm PV} \otimes \Gamma_{\rm PV}]_S \otimes [\Gamma_{\rm PV} \otimes \Gamma_{\rm PV}]_S,$$

i.e. they have the same symmetry as the *piezo-optic* or *elasto-optic* tensor. Reducing this representation into irreducible components $\Gamma(j)$, we obtain the symmetry-restricted form of the linear strain-induced Raman tensors. Evidently, their matrix form is the same as for quadratic electric-field-induced Raman tensors. In centrosymmetric crystals, strain-induced Raman scattering (in any order in the strain) is thus allowed for even-parity modes only.

2.3.5. Spatial-dispersion effects

For $\mathbf{q} = 0$, the normal modes correspond to a homogeneous phonon displacement pattern (all cells vibrate in phase). Phenomenologically, the $\mathbf{q}$-dependence of Raman tensors can be understood as a kind of morphic effect due to the gradients of the displacement field. Developing the contribution of the long-wavelength jth normal mode to the susceptibility in Cartesian components of the displacement of atoms in the primitive cell and their gradients, we obtain

$$\delta\chi^{(j)}_{\alpha\beta}(\mathbf{q}) = \sum_\kappa \left(\frac{\partial\chi_{\alpha\beta}}{\partial u^{(j)}_{\kappa,\gamma}}\right)_0 u^{(j)}_{\kappa,\gamma}(\mathbf{q}) + i\sum_\kappa \left(\frac{\partial\chi_{\alpha\beta}}{\partial(\nabla u^{(j)}_{\kappa,\gamma})_\delta}\right)_0 q_\delta u^{(j)}_{\kappa,\gamma}(\mathbf{q}), \tag{2.3.5.1}$$

where the derivatives are taken at $\mathbf{q} = 0$, and we use the obvious relation $\nabla u^{(j)}_{\kappa,\gamma} = i\mathbf{q}u^{(j)}_{\kappa,\gamma}$.

Transforming to normal coordinates, using (2.3.3.1), we identify the $\mathbf{q} = 0$ intrinsic Raman tensor $\mathbf{R}^{j0}$ of the jth normal mode, explicitly expressed *via* Cartesian displacements of atoms,

$$R^{jo}_{\alpha\beta} \equiv \chi^{(j)}_{\alpha\beta}(0) \equiv \left(\frac{\partial\chi_{\alpha\beta}}{\partial Q_j}\right) = \sum_\kappa \left(\frac{\partial\chi_{\alpha\beta}}{\partial u^{(j)}_{\kappa,\mu}}\right)\frac{e_{\kappa,\mu}(0,j)}{\sqrt{Nm_\kappa}}, \tag{2.3.5.2}$$

and introduce the first-order $\mathbf{q}$-*induced* atomic displacement Raman tensor coefficients $\mathbf{R}^{jq}$:

$$R^{jq}_{\alpha\beta\gamma} \equiv -i\left(\frac{\partial\chi^{(j)}_{\alpha\beta}}{\partial q_\gamma}\right) = -i\left(\frac{\partial^2\chi_{\alpha\beta}}{\partial Q_j\partial q_\gamma}\right) = \sum_\kappa \left(\frac{\partial\chi^{(j)}_{\alpha\beta}}{\partial(\nabla u_{\kappa,\mu})_\gamma}\right)\frac{e_{\kappa,\mu}(0,j)}{\sqrt{Nm_\kappa}}. \tag{2.3.5.3}$$

Hence, to the lowest order in $\mathbf{q}$, the transition susceptibility is expressed as

$$\delta\chi^{(j)}_{\alpha\beta}(\mathbf{q}) \cong \left(R^{j0}_{\alpha\beta} + iR^{jq}_{\alpha\beta\gamma}q_\gamma\right)Q_j(0). \tag{2.3.5.4}$$

In a more general case, spatial dispersion should be considered together with the electro-optic contributions due to the internal macroscopic field $\mathbf{E}$ and its gradients. Assuming the linear susceptibility to be modulated by the atomic displacements Q_j and the macroscopic electric field $\mathbf{E}$ as well as by their gradients ∇Q_j and $\nabla\mathbf{E}$, we can expand the transition susceptibility of the jth phonon mode $Q_j(\mathbf{q})$ to terms linear in $\mathbf{q}$ and formally separate the atomic displacement and electro-optic parts of the Raman tensor [see (2.3.3.15)]:

$$\delta\boldsymbol{\chi}^{(j)}(\mathbf{q}) = (\partial\boldsymbol{\chi}/\partial Q_j)Q_j(\mathbf{q}) + i(\partial\boldsymbol{\chi}/\partial\nabla Q_j)\mathbf{q}Q_j(\mathbf{q}) + (\partial\boldsymbol{\chi}/\partial\mathbf{E})\mathbf{E}^j(\mathbf{q}) + i(\partial\boldsymbol{\chi}/\partial\nabla\mathbf{E})\mathbf{q}\mathbf{E}^j(\mathbf{q}),$$

or concisely

$$\delta\boldsymbol{\chi}^{(j)}(\mathbf{q}) = \mathbf{a}^j(\mathbf{q})Q_j(\mathbf{q}) + \mathbf{b}(\mathbf{q})\mathbf{E}^j(\mathbf{q}),$$

with

$$\mathbf{a}^j(\mathbf{q}) = (\mathbf{a}^{j0} + i\mathbf{a}^{jq}\mathbf{q}), \quad \mathbf{b}(\mathbf{q}) = (\mathbf{b}^0 + i\mathbf{b}^q\mathbf{q}). \tag{2.3.5.5}$$

references