Symmetry Considerations for the Detection of Second-Harmonic Generation in Cuprates in the Pseudogap phase.

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Abstract

A proposal to test the proposed time-reversal and inversion breaking phase in the Pseudogap region of the Cuprate compounds through the variation of Second-harmonic generation intensity with temperature and polarization and angle of incidence is presented.
I. INTRODUCTION

Feibig et al.\(^1\) have discussed the conditions for second harmonic generation proportional to the Time-reversal breaking order parameter for the case of *magnetolectric symmetry*\(^2\), i.e. for the case that Time-reversal Symmetry R is broken and so is Inversion I but their product RI is preserved. Following earlier suggestions\(^3\)\(^,\)\(^4\), ARPES experiments with circularly polarized photons\(^5\) have detected such a phase in the so-called *pseudogap phase* in the phase diagram of a high temperature superconducting compound of the Copper-Oxide (Cu-O) family. Time-reversal is broken due to circulating currents in specific patterns within the unit cell with translational symmetry preserved. If this discovery is correct, it together with the extensive evidence for *Quantum Critical properties* in the normal phase\(^6\) around the doping density for the highest \(T_c\) implies that the basic framework for the theory of the Cuprates is in place. It is therefore very important to verify the discovery by independent experiments. Accordingly, we work out here the symmetry considerations for magneto-electric induced second harmonic generation in the Cuprates.

Many terms in the multipole susceptibility contributes to the second harmonic generation (SHG). The relevant contributions for the processes discussed here come from the magnetic-dipole, \(M_k(2\omega) \propto \chi^m_{ijk}(\omega, \omega, 2\omega)E_i(\omega)E_j(\omega)\), and the electric-dipole, \(E_k(2\omega) \propto \chi^e_{ijk}(\omega, \omega, 2\omega)E_i(\omega)E_j(\omega)\). While the former is generally present in the symmetry of the cuprate compounds, the latter occurs in the predicted pseudogap phase with \(\chi^e_{ijk}\) transforming as an odd tensor under time-reversal. The interference effects due to the simultaneous presence of the two-time-reversal odd tensors \(\chi^m_{ijk}\) and \(\chi^e_{ijk}\) are responsible for the effects discussed here.

II. SYMMETRY OF THE NORMAL PHASE

Most \(Cu-O\) compounds possess a centre of symmetry in the unit-cell. We consider the body-centered tetragonal crystals with symmetry group \(4/mmm(D_{4h})\), denoting the presence of a four-fold axis and a mirror plane orthogonal to this axis and two other mirror planes or orthorhombic crystals with symmetry group \(mmm (D_{2h})\), (three orthogonal mirror planes only). Due to the centre of inversion, the third rank polar tensor \(\chi^e_{ijk}\) arising from electric-dipole effects is zero but the third rank axial tensor \(\chi^m_{ijk}\) arising from magnetic-dipole effects is non-zero. In other words a term in the Free-energy \(\Phi\) of the form

\[
\Phi = \chi^m_{ijk}E_iE_jH_k
\]

exists. Correspondingly a magnetization for applied electric fields

\[
M_k = \chi^m_{ijk}E_iE_j
\]

is non-zero.

We specify the tensors in this paper using the following co-ordinates: The c axis of the crystal coincides with the \(\hat{z}\) direction, a and b crystalline axis (those along the nearest neighbor Cu-Cu vector) are along the \((\hat{x} + \hat{y})/\sqrt{2}\) and \((\hat{x} - \hat{y})/\sqrt{2}\) directions. For the \(4/mmm\) group, three independent components of \(\chi^m_{ijk}\) are non-zero\(^7\). The vector \(\mathbf{M}\) takes the form:
\[
M = \begin{pmatrix}
-x_1^m E_y E_z \\
x_1^m E_z E_x \\
0
\end{pmatrix}
\]  \hspace{1cm} (3)

\[
\chi_1^m \equiv (\chi_{xzy}^m + \chi_{zyx}^m)
\]  \hspace{1cm} (4)

For the \(mmm\) group, six independent elements of \(\chi_{ijk}^m\) exist and all three cartesian components of \(M\) are bilinear in \(E's\). We present detailed results for the \(4/mmm\) crystalline symmetry. Very similar conclusions hold for the \(mmm\) crystalline symmetry.

### III. TIME-REVERSAL BREAKING STATE

Two different phases breaking time-reversal are shown to be possible in the pseudogap phase \(^{3,4}\). The current patterns in these phases in the Cu-O planes are shown in Fig. (1).

One called the \(\Theta_{II}\) phase has the symmetry \(mmm\) (Fig. 1 b). This group is in the \(Magnetoelectric\) class, where both time-reversal (\(R\)) and inversion (\(I\)) are broken but their product is preserved. The other possible phase \(\Theta_I\) (Fig. 1 a) preserves inversion while breaking Time-reversal. It has the symmetry \(4/mmm\). So the effects discussed here do not occur in such a phase.

As will be clear from Fig. (1 b), the point group \(mmm\) has the following elements: the identity, two-fold axis rotation around \(\hat{y}\) (\(C_y\)), the reflections in the \(x-y\) and \(y-z\) planes (\(\sigma_z\) and \(\sigma_x\)), \(RI\), \(R\sigma_y\), \(R\sigma_x\) and \(R\sigma_z\).

In the group \(mmm\), axial tensors of third rank which are invariant under time-reversal \(\chi_{ijk}^{m,(i)}\) are allowed\(^7\). The independent components of \(M\) are

\[
M = \begin{pmatrix}
\chi_x^m E_y E_z \\
\chi_y^m E_z E_x \\
\chi_z^m E_x E_y
\end{pmatrix}
\]  \hspace{1cm} (5)

where \(\chi_{jki}^m + \chi_{kji}^m = \chi_i^m\) and \(i, j, k\) run over \(x, y, z\). But more importantly, polar-tensors of odd-rank \(\chi_{ijk}^{e(\cdot)}\), which change sign under time-reversal are also allowed. So a Polarization vector of the form

\[
P = \begin{pmatrix}
\chi_1^{e(x)} E_x E_y \\
\chi_{xy}^{e(e)} E_x^2 + \chi_{xyz}^{e(e)} E_x^2 \\
\chi_2^{e(e)} E_z E_y
\end{pmatrix}
\]  \hspace{1cm} (6)

is allowed. Here \(\chi_1^{e(x)} = \chi_{yxx}^{e(x)} + \chi_{yxy}^{e(x)}\) and \(\chi_2^{e(e)} = \chi_{yzz}^{e(e)} + \chi_{zyz}^{e(e)}\). These \(\chi's\) are expected to be proportional to the order parameter \(\Theta_{II}\).

From these we can construct the relevant part of the Poynting vector \(S\):

\[
S = \frac{\partial^2 P}{\partial t^2} + \nabla \times \frac{\partial M}{\partial t}
\]  \hspace{1cm} (7)
The SHG intensity is $I \propto |S|^2$. As shown below, interesting effects arise in experimental geometries in which both $\chi^e(c)$ and $\chi^m$ are used and interfere. Then effects linear in the magnetoelectric order parameter are observable. If light is propagated in the sample along any of the axes, $\nabla \times \mathbf{M} = 0$. Then only the electric-dipole susceptibility contributes to the SHG and $I \propto |\chi^e|^2$ which is in turn proportional only to the square of the order parameter.

We fix the axes with respect to the crystal as in Fig. (2). For an arbitrary direction of incidence, Figure 2 shows the triad form by the propagation vector $\mathbf{q}$ (specified by the polar angle $\theta$ and the azimuthal angle $\phi$), and the components of the polarization along the orthogonal directions $\hat{e}_{xy}$ in the x-y plane and $\hat{e}_{qz}$ in the q-z plane. To maximize the second term in Eq. (7) we chose a polar incidence angle $\theta = \pi/4$. 

FIG. 1. Current patterns for the time-reversal breaking states proposed in Ref.3,4.
Fig. 2. Geometry of incident light vector \( \mathbf{q} \). The axes are fixed to the crystal: \( \hat{x} \) and \( \hat{y} \) are rotated \( \pi/4 \) with respect to the crystalline axis \( a \) and \( b \) as explained in the text.

For light linearly polarized along the direction \( \mathbf{E} = E \hat{e}_{qz} \),

\[
\mathbf{S} = E^2 \omega \begin{pmatrix}
\omega \sin \phi s_1^e \\
\omega \cos \phi s_2^e - |\mathbf{q}| \sin \phi \cos \phi (\chi_x^m + \chi_y^m + \chi_z^m)/(2\sqrt{2}) \\
\omega \sin \phi s_3^e - |\mathbf{q}|(\cos^2 \phi \chi_y^m + \sin^2 \phi \chi_x^m)/2
\end{pmatrix}
\]

where,

\[
s_1^e = (\cos \phi (\chi_1^e - \chi_2^e) - \cos^2 \phi \chi_{xx}^e - \sin \phi \chi_{xy}^e - \chi_{zy}^e)/(2\sqrt{2})
\]

\[
s_2^e = -(\chi_{zy}^e + \cos^2 \phi \chi_{xy}^e + \sin^2 \phi (\chi_{yy}^e - \chi_1^e))/2
\]

\[
s_3^e = (\cos \phi (\chi_1^e + \chi_2^e) - \cos^2 \phi \chi_{xx}^e - \sin \phi \chi_{xy}^e - \chi_{zy}^e)/(2\sqrt{2})
\]

The component are given in the basis \( (\hat{q}, \hat{e}_{xy}, \hat{e}_{qz}) \).

\[
I \propto E^4 \omega^2 \left[ \omega^2 (\sin^2 \phi |s_1^e|^2 + |s_3^e|^2) + \cos^2 \phi |s_2^e|^2 \right]
+ |\mathbf{q}|^2 (|\sin \phi \cos \phi (\chi_x^m + \chi_y^m + \chi_z^m)|^2/8 + |\cos^2 \phi \chi_y^m + \sin^2 \phi \chi_x^m|^2)
- \omega |\mathbf{q}| \sin \phi (\cos^2 \phi \Re s_2^e (\chi_x^m + \chi_y^m + \chi_z^m)*/2\sqrt{2} + \Re s_3^e (\cos^2 \phi \chi_y^m + \sin^2 \phi \chi_x^m))/2\right]
\]

The \( \chi \)'s defined below are complex and \( \chi^* \) denotes complex conjugation. The last term in Eq. (10) is linear in both \( \chi^m \) and \( \chi^e \) and is therefore proportional to the order parameter.

For an incident light linearly polarized, \( \mathbf{E} = E \hat{e}_{xy} \),

\[
\mathbf{S} = E^2 \omega \begin{pmatrix}
\omega \sin \phi s_1^e \\
\omega \cos \phi s_2^e + |\mathbf{q}| \sin \phi \cos \phi \chi_z^m/\sqrt{2} \\
\omega \sin \phi s_3^e
\end{pmatrix}
\]

where,

\[
s_1^e = (\sin \phi \cos \phi \chi_1^e - \sin^2 \phi \chi_{yy}^e - \cos^2 \phi \chi_{xy}^e)/\sqrt{2}
\]

\[
s_2^e = -(\sin^2 \phi \chi_1^e + \chi_{xx}^e) + \cos^2 \phi \chi_{yy}^e
\]
It is interesting to consider circularly polarized light with right \( E_+ = -1/\sqrt{2}(E_{xy} + iE_{zq}) \) and left \( E_- = 1/\sqrt{2}(E_{xy} - iE_{zq}) \) polarizations and evaluate the intensity \( I \propto |S|^2 \) for each case. This gives

\[
I \propto |E_\pm|^4 \omega^2 (\omega^2 |\psi(\phi)^e|^2 + |q|^2 |\psi(\phi)^m|^2 \pm \cos(\phi) Re(i\omega q|\psi_{int}(\phi)^e(\psi_{int}(\phi)^m)*) \] (13)

Again the last term is the interesting term as it is linear in both \( \chi^m \) and \( \chi^e \) and is therefore proportional to the order parameter. Its sign is changed on reversing the polarization of the light or by reversing time (i.e. by reversing the domains or reversing the direction of propagation for a fixed domain i.e. changing \( \phi \) to \( \pi + \phi \)). For \( \cos \phi = \pm 1 \), that is when \( q \) belongs to the broken symmetry plane \( \hat{y} \), the difference between both circular polarization is maximized. For this case,

\[
|\psi(0)^e|^2 = |\chi_2^e|^2 + |\chi_1^e|^2 + |\chi_{yy}^e|^2 + \frac{1}{2} |\chi_{xy}^e + \chi_{zy}^e|^2 \] (14)

\[
2|\psi(0)^m|^2 = |\chi_y^m|^2 + |\chi_x^m + \chi_z^m|^2
\]

\[
\psi_{int}(\pi/2)^e(\psi_{int}(\pi/2)^m)^* = (\chi_{xy}^e + \chi_{zy}^e - 2\chi_{yy}^e)(\chi_x^m + \chi_z^m)^* + (\chi_1^e + \chi_3^e)(\chi_2^m)^*
\]

In summary we have determined the SHG intensities, as a function of polarization and direction of the incident light, for different group symmetries corresponding to the normal and time-reversal breaking symmetry states. In all the states there is a contribution to the SHG coming from the magnetic-dipole terms but the electric-dipole contribution appears only when the inversion and time-reversal are broken with their product preserved, as in the \( \Theta_{II} \) phase. The interference of these two terms produce linear terms in both \( \chi^m \) and \( \chi^e \) and therefore proportional to the order parameter. This term change sign reversing the domains \( \Theta_{II} \) to \( -\Theta_{II} \) or changing the direction of incident light by the operation \( q \to \sigma_y \sigma_x q \) (which has the effect of changing \( \phi \) to \( \phi + \pi \)). The interference term also changes sign on changing from left to right circularly polarized light.

The presence of many different \( \Theta_{II} \) domains within the spot size of the incident beam will blur this effect. ARPES experiments\(^5\) indicate domains to be of \( O(100 \text{ microns}) \).

The proposed experiment are a rather thorough test of the symmetries of the predicted phase because they rely on broken R and \( \sigma_y \) (or \( \sigma_x \)) but their product preserved below the pseudogap temperature in the cuprates. Breaking reflection symmetry alone would not produce the predicted effects in Second-harmonic generation, while the ARPES experiment\(^5\) is in principle compatible\(^4\) with breaking some reflection symmetries alone. Some other experiments using resonant x-ray absorption and diffraction have also been proposed \(^8\).

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