An introduction to the optical spectroscopy of solids

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Outline

1. Optical constants and their relations
   (Optical constants, Kramers-Kronig transformation, intra- and interband transitions)

2. Drude model of simple metal (example of application)

3. Spectroscopy of correlated electrons

4. THz time domain spectroscopy (Particularly optical pump, THz probe)
References

• C. Kittle, Solid State Physics

• F. Wooten, Optical properties of solids (Academic Press, 1972)

• M. Dressel and G. Grüner, Electrodynamics of solids (Cambridge University Press, 2002)
Optical spectroscopy is a primary tool to probe the charge dynamics and quasiparticle excitations in a material.

D. Basov, et al.
Rev. Mod. Phys.
(2011)

Units: 1 eV = 8065 cm$^{-1}$ = 11400 K
1.24 eV = 10000 cm$^{-1}$
The electrodynamical properties of solids described by a number of so-called “optical constants”: complex refractive index, or complex dielectric constants, or complex conductivity.

Those optical constants could be probed either directly (ellipsometry, ultrfast laser-based time domain terahertz spectroscopy,...) or indirectly (reflectance measurement over broad frequencies).
Optical constants

Consider an electromagnetic wave in a medium

\[ E_y = E_0 e^{i(qx - \omega t)} = E_0 e^{i\omega(x/v - t)} = E_0 e^{i\omega(\frac{nx}{c} - t)} \]

where \( v \equiv \frac{\omega}{q} = \frac{c}{n(\omega)} \), \( n(\omega) \): refractive index

If there exists absorption, \( K \): attenuation factor

\[ E_y = E_0 e^{\frac{-\omega K x}{c} - i\omega(\frac{nx}{c} - t)} \]

Intensity

\[ I \propto E_y^2 = E_0^2 e^{-\frac{2\omega K x}{c}} \]

Introducing a complex refractive index:

\[ N(\omega) \equiv n(\omega) + iK(\omega) \]

\[ E_y = E_0 e^{i\omega\left(\frac{N(\omega)x}{c} - t\right)} \]
Reflectivity

\[ \frac{E_{\text{ref}}}{E_{\text{in}}} = r = r(\omega)e^{i\theta(\omega)} \]

\[ = \frac{n + iK - 1}{n + iK + 1} = \sqrt{\frac{(n - 1)^2 + K^2}{(n + 1)^2 + K^2}} e^{i\theta(\omega)} \]

\[ R = \left| \frac{E_{\text{ref}}}{E_{\text{in}}} \right|^2 = \left| r(\omega) \right|^2 = \frac{(n - 1)^2 + K^2}{(n + 1)^2 + K^2} \]

\[ \tan \theta = \frac{2K}{n^2 + K^2 - 1} \]

If \( n, K \) are known, we can get \( R, \theta \); vice versa.
Dielectric function

\[ D(q, \omega) \equiv \varepsilon(q, \omega)E(q, \omega) \]

\( \text{photon, } q \to 0, \varepsilon = \varepsilon(\omega, q \to 0) = \varepsilon(\omega) \)

\[ \therefore \sqrt{\varepsilon(\omega)} = N(\omega) \]

\[ \Rightarrow \varepsilon(\omega) \equiv \varepsilon_1(\omega) + i\varepsilon_2(\omega) = (n(\omega) + iK(\omega))^2 \]

\[ \varepsilon_1(\omega) = n^2(\omega) - K^2(\omega) \]

\[ \varepsilon_2(\omega) = 2n(\omega) \cdot K(\omega) \]

\[ n = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)} \]

\[ k = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)} \]

Infrared
\( q=2\pi/\lambda \sim 10^{-4} \text{ Å}^{-1} \)
conductivity

$$\sigma = \sigma_1(\omega) + \sigma_2(\omega)$$

By electrodynamics, $$\varepsilon(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}$$

In a solid, considering the contribution from ions or from high energy electronic excitations

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{4\pi i \sigma(\omega)}{\omega}$$
Now, we have several pairs of optical constants:

\[
\begin{align*}
    &n(\omega), \ K(\omega) \\
    &R(\omega), \ \theta(\omega) \\
    &\varepsilon_1(\omega), \ \varepsilon_2(\omega) \\
    &\sigma_1(\omega), \ \sigma_2(\omega)
\end{align*}
\]

Usually, only \(R(\omega)\) can be measured experimentally.
Kramers-Kronig relation

-- the relation between the real and imaginary parts of a response function.

For optical reflectance

\[ r(\omega) = \sqrt{R(\omega)}e^{i\theta} \]
\[ \Rightarrow \ln r(\omega) = (1/2)\ln R(\omega) + i\theta \]

Low-\(\omega\) extrapolations:

- Insulator: \(R\sim\) constant
- Metal: Hagen-Rubens
- Superconductor: two-fluids model

High-\(\omega\) extrapolations:

- \(R\sim\omega^p\) (\(p\sim0.5-1\), for intermediate region)
- \(R\sim\omega^n\) (\(n=4\), above interband transition)
Reflectivity measurement
FTIR
In-situ overcoating technique

FT-IR spectrometer

In situ evaporation

\[
\left( \frac{R_g}{R_r} \right) \left( \frac{R_{gs}}{R_r} \right)^{-1} = \frac{R_g}{R_{gs}}
\]

C. C. Homes et al.
Applied Optics 32,2976(1993)
Infrared light **cannot** be absorbed directly by electron-hole excitation.

(a) **Impurity-assisted absorption**

(b) **Boson-assisted absorption**

Holstein process, if phonons are involved.
简单金属：Drude model

\[ \sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau} = \frac{\omega_D^2}{4\pi} \frac{1}{1/\tau - i\omega} \]

\[ \varepsilon(\omega) = \varepsilon_\infty + \frac{4\pi i}{\omega} \sigma(\omega) \]

\[ \Rightarrow \varepsilon_1 = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + 1/\tau^2} \]

\[ \varepsilon_2 = \frac{4\pi \sigma_1}{\omega} = \frac{\omega_p^2 \tau}{\omega} \frac{1}{1 + \omega^2 \tau^2} \]

\[ \text{Im}\left\{ \frac{-1}{\varepsilon(\omega)} \right\} = \frac{\omega_p^2 \omega / \tau}{(\omega^2 - \omega_p^2)^2 + \omega^2 \tau^{-2}} \]

\[ \omega_p' = \omega_p / \sqrt{\varepsilon_\infty} \]

\[ \int_0^\infty \sigma_1(\omega) d\omega = \frac{\omega_p^2}{8} \]
举例: Parent compound 1T-TiSe2

- 1T-TiSe2 was one of the first CDW-bearing materials

- Broken symmetry at 200 K with a 2x2x2 superlattice

- Semiconductor or semimetal?

Ti: $3d^24s^2$

Se: $4s^24p^4$

related to the CDW mechanism

Ti : 3d band fully empty ?

Se: 4p band fully occupied?
Band structure and lattice instability of TiSe$_2$

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(Received 23 June 1977)

Ti: 3d$^2$4s$^2$

Se: 4s$^2$4p$^4$

Ti: 3d band

Se: 4p band

FIG. 1. Energy-band structure of TiSe$_2$ in the local exchange and correlation model.
The electron-hole coupling acts to mix the electron band and hole band that are connected by a particular wave vector.
**TiSe$_2$ single crystal**

G. Li et al., PRL (07a)
Free carriers with very long relaxation time exist in the CDW gapped state

FS is not fully gapped??
\[ \epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{i=1}^{2} \frac{S_i^2}{\omega_i^2 - \omega^2 - i\omega/\tau_i}. \] (1)

It contains a Drude term and two Lorentz terms, which approximately capture the contributions by free carriers and interband transitions. As shown in the inset of
Exciton-driven CDW

\[ \omega_p^2 = 4\pi e^2 \left( \frac{n_h}{m_h} + \frac{n_e}{m_e} \right) \]

\[ R_H = \frac{1}{e} \left( \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2} \right), \]

\[ \sigma = e(n_h \mu_h + n_e \mu_e) \]

G. Li et al., PRL (07a)
Simple metal

High-\(T_c\) cuprates

\[
R \quad \omega \ (\text{cm}^{-1})
\]

\[
R \quad \omega \ (\text{cm}^{-1})
\]

- gold
- YBCO
- Bi2212

Simple metal

High-\(T_c\) cuprates
Electron correlations reflected in optical conductivity

**Simple metal**

Correlation effect: reducing the kinetic energy of electrons, or Drude spectral weight.

\[ \omega_p^2 = \frac{4\pi Ne^2}{m_b} \]

**Correlated metal**

\[ \omega_p^{Tot} = \omega_p^{Drude} + \omega_p^{MIR} = \frac{4\pi Ne^2}{m^*} \]

\[ \frac{m^*}{m_b} = \frac{\omega_p^{Tot} \omega_p^{Drude}}{\omega_p^{Drude} \omega_p^{Drude}} \]
\[
\frac{K_{\text{exp}}}{K_{\text{band}}} = \frac{\int_0^{\omega_{\text{opt}}} \sigma_1(\omega) d\omega}{\int_0^{\omega_{\text{band}}} \sigma_1(\omega) d\omega}
\]

\[
\frac{K_{\text{exp}}}{K_{\text{band}}} = \frac{\omega_p^2}{\omega_p^2 + (\omega_p^\text{MIR})^2}
\]

Q M Si, Nature Physics 2009
Table 1| The ratio of the experimental kinetic energy $K_{\text{exp}}$ extracted from optical measurements, as described in ref. 27, and $K_{\text{LDA}}$ provided by band-structure calculations.

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>$T_{c \text{max}}$</th>
<th>$K_{\text{exp}}/K_{\text{LDA}}$ at $T_{c \text{max}}$</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$_{2-x}$Ce$_x$CuO$_4$</td>
<td>25</td>
<td>0.3</td>
<td>31</td>
</tr>
<tr>
<td>Pr$_{2-x}$Ce$_x$CuO$_4$</td>
<td>25</td>
<td>0.32</td>
<td>31</td>
</tr>
<tr>
<td>La$_{2-x}$Sr$_x$CuO$_4$</td>
<td>40</td>
<td>0.25</td>
<td>31</td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>3$O$</em>{7-x}$</td>
<td>93.5</td>
<td>0.4</td>
<td>8</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CaCu$<em>2$O$</em>{8+y}$</td>
<td>94</td>
<td>0.45</td>
<td>*</td>
</tr>
<tr>
<td>FeSCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaFePO</td>
<td>7</td>
<td>0.5</td>
<td>27</td>
</tr>
<tr>
<td>Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$</td>
<td>23</td>
<td>0.35–0.5</td>
<td>27, **</td>
</tr>
<tr>
<td>Ba$_{1-x}$K$_x$Fe$_2$As$_2$</td>
<td>39</td>
<td>0.3</td>
<td>43</td>
</tr>
<tr>
<td>Exotic SCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeCoIn$_5$</td>
<td>2.3</td>
<td>0.17</td>
<td>44, 45</td>
</tr>
<tr>
<td>Sr$_2$RuO$_4$</td>
<td>1.5</td>
<td>0.4</td>
<td>27</td>
</tr>
<tr>
<td>$\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$</td>
<td>12</td>
<td>0.4</td>
<td>46</td>
</tr>
<tr>
<td>Electron-phonon SCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgB$_2$</td>
<td>40</td>
<td>0.9</td>
<td>27</td>
</tr>
<tr>
<td>K$<em>3$C$</em>{60}$</td>
<td>20</td>
<td>0.96</td>
<td>47, 48</td>
</tr>
<tr>
<td>Rb$<em>3$C$</em>{60}$</td>
<td>30</td>
<td>0.9</td>
<td>47, 48</td>
</tr>
</tbody>
</table>

*D. van der Marel et al., unpublished; **A. Schafgans et al., unpublished.
Hubbard U physics: \( \rho(\omega) \)

\[
\rho(\omega) \equiv -\frac{1}{\pi} \sum_k \text{Im} G(k, \omega + i0^+) 
\]

FIG. 30. Local spectral density \( \pi D \rho(\omega) \) at \( T=0 \), for several values of \( U \), obtained by the iterated perturbation theory approximation. The first four curves (from top to bottom, \( U/D = 1, 2, 2.5, 3 \)) correspond to an increasingly correlated metal, while the bottom one (\( U/D = 4 \)) is an insulator.

served. As \( T \) is lowered, there is an enhancement of the spectrum at intermediate frequencies of order 0.5 eV; more notably, a sharp low-frequency feature emerges that extends from 0 to 0.15 eV.
Sum rule

f-sum rule:
\[ \int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi ne^2}{2m_e} = \omega_p^2 / 8 \]

It has the explicit implication that at energies higher than the total bandwidth of a solid, electrons behave as free particles.

Kubo partial sum-rule:
\[ \int_0^W \sigma_1(\omega) d\omega = W_K = \frac{\pi e^2}{2N} \sum_k \nabla_{k_x}^2 \epsilon_k n_k \]

The upper limit of the integration is much larger than the bandwidth of a given band crossing the Fermi level but still smaller than the energy of interband transitions. For \( \epsilon_k = k^2 / 2m_e \), the Kubo sum rule reduces to the f-sum rule.

\( W_K \) depends on \( T \) and on the state of the system because of \( n_k \)--"violation of the conductivity sum rule", first studied by Hirsch.

In reality, there is no true violation: the change of the spectral weight of a given band would be compensated by an appropriate change in the spectral weight in other bands, and the total spectral weight over all bands is conserved.
Extended Drude Model

Drude Model

\[ \sigma(\omega) = \frac{\omega_p^2}{4\pi} \frac{1}{1/\tau - i\omega} \]

Let \( M(\omega,T) = 1/\tau(\omega,T) - i\omega\lambda(\omega,T) \)

\[ \sigma(\omega,T) = \frac{\omega_p^2}{4\pi} \frac{1}{M(\omega,T) - i\omega} \]

\[ = \frac{\omega_p^2}{4\pi} \frac{1}{1/\tau(\omega,T) - i\omega[1 + \lambda(\omega,T)]} \]

\[ = \frac{1}{4\pi} \frac{\omega^*_p}{1/\tau^*(\omega,T) - i\omega} \]

1/\(\tau(\omega,T)\): Frequency dependent scattering rate

\( \lambda \): Mass enhancement \( m^* = m(1 + \lambda) \)

\[ 1/\tau(\omega,T) = \left( \omega_p^2 / 4\pi \right) \text{Re}[1/\sigma(\omega,T)] \]

\[ m^*/m = 1 + \lambda(\omega) = \left( \omega_p^2 / 4\pi\omega \right) \text{Im}[1/\sigma(\omega,T)] \]

e.g. Marginal Fermi Liquid model:

\[ M(\omega,T) = 1/\tau(\omega,T) - i\omega\lambda(\omega,T) \]

\[ = g^2N^2(0) \left( \frac{\pi}{2} x + i\omega \ln \frac{x}{\omega_c} \right) \]

Where \( x = \max(|\omega|, T) \),

or \( x = (\omega^2 + \alpha(\pi T)^2)^{1/2} \)
The extended Drude model in terms of optical self-energy

\[
\sigma(\omega, T) = \frac{\omega_p^2}{4\pi} \frac{1}{(\gamma(\omega, T) - i\omega)}
\]

According to Littlewood and Varma,

\[
\gamma(\omega) = -2i\Sigma^{op}
\]

\[
= -2i[\Sigma_1(\omega) + i\Sigma_2(\omega)]
\]

Optical self-energy

Relation to the $1/\tau(\omega)$ and $m^*/m$

\[
\gamma_1(\omega) = 1/\tau(\omega) = 2\Sigma_2
\]

\[
\gamma_2(\omega) = \omega(1 - m^*/m) = -2\Sigma_1
\]
Bi2212

Hwang, Timusk, Gu,
The electron-boson (phonon) interaction

\[ 1/\tau(\omega) = \frac{2\pi}{\omega} \int_0^\infty d\Omega (\omega - \Omega) \alpha^2_{tr}(\Omega) F(\Omega) \]

At 0K, based on Allen's formula

\[ \alpha^2 F(\omega) = \frac{\omega_p^2 \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \]

\( \omega_0 = 500 \text{ cm}^{-1} \)

\( \gamma = 100 \text{ cm}^{-1} \)

\( \omega_p^2 = 50000 \text{ cm}^{-2} \)

T=0 K

P.B. Allen 1971
Allen’s formula for the scattering rate in the superconducting state

\[ \frac{1}{\tau(\omega)} = \frac{2\pi}{\omega} \int_0^{\omega-2\Delta} d\Omega (\omega - \Omega) \alpha^2 F(\Omega) E \sqrt{1 - \frac{4\Delta^2}{(\omega - \Omega)^2}} \]

P.B. Allen 1971

\( E(x) \) is the second kind elliptic integral

FIG. 9. Model spectral function \( \alpha^2 F(\omega) \) (thin line) is used to calculate the scattering rate \( 1/\tau_{\text{cal}}(\omega) \) from Eq. (13). For \( \Delta = 0 \) the calculated scattering rate resembles \( 1/\tau(\omega) \) of underdoped \( \text{YBa}_2\text{Cu}_3\text{O}_{6.60} \) (Fig. 7). However, for finite values of the gap the calculated scattering rate resembles \( 1/\tau(\omega) \) of optimally doped \( \text{YBa}_2\text{Cu}_3\text{O}_{6.95} \); there is an overshoot following the suppressed region (Fig. 7).
Optical spectra of a superconductor

$T=0$, London electrodynamics gives

$$\sigma = \frac{1}{8} \omega_{ps}^2 d(\omega) + i \omega_{ps}^2 / 4\pi \omega \quad \Rightarrow \quad \frac{1}{\lambda_L^2} = \frac{8}{c^2} \int_0^\infty (\sigma_1^n - \sigma_1^s) d\omega \quad \text{or} \quad \frac{1}{\lambda_L^2} = \frac{4\pi}{c^2} \omega \sigma_2(\omega)$$

Ferrell-Glover-Tinkham sum-rule: missing area is equal to the superconducting condensate.

dirty limit: $\xi>1 \iff 2\Delta<\Gamma$
Absorption starts at $2\Delta$.

clean limit: $\xi<1 \iff 2\Delta>\Gamma$
Absorption starts at $2\Delta+\Omega$.

$pippard coherence length$
$\xi=v_F/\pi\Delta, \Gamma=1/\tau=v_F/l$
Coherent factors and characteristic spectral structures in density wave or superconductors

$$\alpha_s = \int |M|^2 F(\Delta, E, E + \hbar \omega) N_s(E) N_s(E + \hbar \omega) [f(E) - f(E + \hbar \omega)] dE$$

$$H_1 = \sum_{k\sigma, k\sigma'} B_{k'\sigma', k\sigma} C_{k'\sigma'}^{*} C_{k\sigma}$$

$B_{k'\sigma', k\sigma}$ 和 $B_{-k-\sigma, -k'-\sigma'}$ 的叠加是相干的

参看 Tinkham 超导电性的教科书

$$F(\Delta, E, E') = \frac{1}{2} (1 \mp \frac{\Delta^2}{EE'})$$

$$\frac{\sigma^S_1}{\sigma^N_1} = \frac{1}{\hbar \omega} \int_{-\infty}^{\infty} \frac{|E(E + \hbar \omega) \mp \Delta^2|}{(E^2 - \Delta^2)^{1/2}[(E + \hbar \omega)^2 - \Delta^2]^{1/2}} [f(E) - f(E + \hbar \omega)] dE$$
Gap feature in density waves

URu2Si2

E. Fawcett et al.: Spin-density-wave antiferromagnetism in chromium alloys
Gap structure in superconductors

$\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$

G. Li et al PRL 08

Cuprates, Homes data
Coherent peak below Tc

T. Fischer et al PRB 2010


铁基超导体的THz数据与NMR不同？S+-配对？
Optik IFS113v/ IFS66v

SIDE LOADING SAMPLE IN VACUUM
Optical measurement under magnetic field

Bruker 113v spectrometer

(10 Tesla split coils from Cryomagnetic Inc.)

Liquid He
Josephson Plasma edge in K0.75Fe1.75Se2 from nanoscale phase separation

Effect of magnetic field:

Magneto-Optical Reflectivity in EuB6

Pump-probe experiment based on femtosecond laser

Quasiparticle relaxation after optical pump
飞秒激光
太赫兹天线
光阑
分光镜
样品、恒温器或磁体系统

计算机
锁相放大器

平衡探测器
ZnTe
\( \lambda/4 \)

渥拉斯棱镜
硅分光镜

太赫兹时域光谱系统原理图
THz time domain spectroscopy
Femtosecond laser can selectively excite certain modes of correlated electronic systems, and controllably push materials from one ordered phase to another.
In the equilibrium low-temperature superconducting state, a Josephson plasma edge is clearly visible, reflecting the appearance of coherent transport. This edge is fitted with a two-fluid model (continuous line). Above \(T_c\), incoherent ohmic transport is reflected in a featureless conductivity. (B) Static \(c\)-axis reflectance of \(\text{LSCO}_{0.18}\) at 10 K. The optical properties are those of a nonsuperconducting compound down to the lowest temperatures. (C) Transient \(c\)-axis reflectance of \(\text{LSCO}_{1/8}\), normalized to the static reflectance. Measurements are taken at 10 K, after excitation with IR pulses at 16 \(\mu\)m wavelength. The appearance of a plasma edge at 60 \(\text{cm}^{-1}\) demonstrates that the photoinduced state is superconducting.
Thanks!