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)

I. Optical constants and their relations

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 $v \equiv \omega/q = c/n(\omega)$, $n(\omega)$: refractive index

If there exists absorption,

$$E_{y} = E_{0}e^{-\frac{\omega Kx}{c}}e^{i\omega(\frac{nx}{c}-t)}$$

K: attenuation factor

Intensity
$$\mathbf{I} \propto E_y^2 = E_0^2 e^{-\frac{2\omega Kx}{c}}$$

Introducing a complex refractive index:

$$E_{y} = E_{0}e^{i\omega(\frac{N(\omega)x}{c}-t)}$$

$$N(\omega) \equiv n(\omega) + iK(\omega)$$

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Reflectivity

$$\frac{E_{ref}}{E_{in}} \equiv r = r(\omega)e^{i\theta(\omega)}$$
$$= \frac{n + iK - 1}{2} = \sqrt{(n-1)^2 + K^2}$$

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



$$R = |E_{ref} / E_{in}|^{2} = |r(\omega)|^{2} = \frac{(n-1)^{2} + K^{2}}{(n+1)^{2} + K^{2}} \qquad n = \frac{1-R}{1+R-2R^{1/2}\cos\theta}$$
$$tg\theta = \frac{2K}{n^{2} + K^{2} - 1} \qquad k = \frac{-2R^{1/2}\sin\theta}{1+R-2R^{1/2}\cos\theta}$$

If n, K are known, we can get R, θ ; vice versa.

Dielectric function

$$D(q,\omega) \equiv \varepsilon(q,\omega)E(q,\omega)$$

photon, $q \to 0, \varepsilon = \varepsilon(\omega, q \to 0) = \varepsilon(\omega)$

$$0 \quad \pi/a \sim 1 \text{\AA}^{-1}$$
Infrared
q=2 $\pi/\lambda \sim 10^{-4} \text{\AA}^{-1}$

$$\because \sqrt{\varepsilon(\omega)} = N(\omega)$$

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

$$\begin{cases} \varepsilon_1(\omega) = n^2(\omega) - K^2(\omega) \\ \varepsilon_2(\omega) = 2n(\omega) \cdot K(\omega) \end{cases} \text{ or } \begin{aligned} n = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)} \\ k = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)} \end{aligned}$$

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:

$$\begin{cases} n(\omega), K(\omega) \\ R(\omega), \theta(\omega) \\ \epsilon_1(\omega), \epsilon_2(\omega) \\ \sigma_1(\omega), \sigma_2(\omega) \end{cases}$$

Usually, only $R(\omega)$ can be measured experimentally.

Kramers-Kronig relation

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

$$\alpha_{1}(\omega) = \frac{2}{\pi} P \int_{0}^{+\infty} \frac{\omega' \alpha_{2}(\omega') d\omega'}{\omega'^{2} - \omega^{2}}$$
$$\alpha_{2}(\omega) = \frac{-2\omega}{\pi} P \int_{0}^{\infty} \frac{\alpha_{1}(\omega') d\omega'}{\omega'^{2} - \omega^{2}}$$

For optical reflectance

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

$$\implies \theta = \frac{\omega}{\pi} P \int_0^\infty \frac{\ln R(\omega')}{\omega^2 - {\omega'}^2} d\omega'$$

Low- ω extrapolations:

Insulator: R~ constant

Metal: Hagen-Rubens

Superconductor: two-fluids model

High- ω extrapolations:

R~ ω^{-p} (p~0.5-1, for intermedate region)

R~ ω^{-n} (n=4, above interband transition)

Reflectivity measurement



FTIR



In-situ overcoating technique

FT-IR spectrometer



In situ evaporation



C. C. Homes *et al.* Applied Optics 32,2976(1993)

Fig. 5. Irregular piece broken from a crystal of ${\rm SrTiO}_3$ used to measure the spectra in Fig. 6.

1mm100kV 328E1 5488/00

Interband transition



Kubo-Greenwood formula

$$\varepsilon_{2}(\omega) = \frac{8\pi^{2}e^{2}}{m^{2}\omega^{2}} J(\hbar\omega) |\vec{p}_{vc}(\hbar\omega)|^{2}$$

$$\sigma_1(\omega) = \frac{1}{4\pi} \omega \varepsilon_2(\omega)$$

Intraband transition



简单金属: Drude model

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

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

$$\Rightarrow \varepsilon_{1} = \varepsilon_{\infty} - \frac{\omega_{p}^{2}}{\omega^{2} + 1/\tau^{2}}$$
$$\varepsilon_{2} = \frac{4\pi\sigma_{1}}{\omega} = \frac{\omega_{p}^{2}\tau}{\omega} \frac{1}{1 + \omega^{2}\tau^{2}}$$

$$\operatorname{Im}\left\{\frac{-1}{\varepsilon(\omega)}\right\} = \frac{\omega_p^{2}\omega/\tau}{(\omega^{2} - \omega_p^{2})^{2} + \omega^{2}\tau^{-2}}$$
$$\omega_p = \omega_p / \sqrt{\varepsilon_{\infty}}$$

$$\int_{0}^{\infty} \sigma_{1}(\omega) d\omega = \frac{\omega_{p}^{2}}{8}$$



举例: Parent compound 1T-TiSe2

Se: 4s²4p⁴

- 1T-TiSe2 was one of the first CDW-bearing materials
- Broken symmetry at 200 K with a 2x2x2 superlattice
- Semiconductor or semimetal?





Se: 4p band fully occupied?

Band structure and lattice instability of TiSe₂

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FIG. 1. Energy-band structure of TiSe₂ in the local exchange and correlation model.

Excitonic Phases W. Kohn, PRL 67



FIG. 1. The insulating side. (a) Energy bands and exciton band of the normal insulator. (b) The new energy bands after the first excitonic transition for successive values of the external parameter (e.g., pressure). (c) The second excitonic instability.



FIG. 2. The metallic side. (a) Energy bands of the normal semimetal. (b) Energy bands after the first Overhauser transition for two different directions of k.



FIG. 3. The excitonic phases. (a) Succession of phases, at $T = 0^{\circ}$, for different values of α ; *m*, metallic; *i*, insulating. The dotted interval contains an infinity of *m* and *i* phases. (b) Total phase diagram, showing an infinity of nested phases.

The electron-hole coupling acts to mix the electron band and hole band that are connected by a particular wave vector.





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



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



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.

Correlated metal





$$K_{exp}/K_{band} = \frac{\int_0^{\omega_{opt}} \sigma_1(\omega) d\omega}{\int_0^{\omega_{band}} \sigma_1(\omega) d\omega}$$

$$K_{exp}/K_{band} = \frac{\omega_p^2}{\omega_p^2 + (\omega_p^{MIR})^2}$$

Q M Si, Nature Physics 2009

Superconductor	T _{c max}	K_{exp}/K_{LDA} at T_{cmax}	Refs
CuSCs			
Nd _{2-x} Ce _x CuO ₄	25	0.3	31
Pr _{2-x} Ce _x CuO ₄	25	0.32	31
La _{2-x} Sr _x CuO ₄	40	0.25	31
YBa ₂ Cu ₃ O _{7-x}	93.5	0.4	8
$Bi_2Sr_2CaCu_2O_{8+\delta}$	94	0.45	*
FeSCs			
LaFePO	7	0.5	27
Ba(Fe _{1-x} Co _x) ₂ As ₂	23	0.35-0.5	27,**
Ba _{1-x} K _x Fe ₂ As ₂	39	0.3	43
Exotic SCs			
CeCoIn₅	2.3	0.17	44,45
Sr ₂ RuO ₄	1.5	0.4	27
κ-(BEDT-TTF) ₂ Cu(SCN) ₂	12	0.4	46
Electron-phonon SCs			
MgB ₂	40	0.9	27
K₃C ₆₀	20	0.96	47,48
Rb ₃ C ₆₀	30	0.9	47,48

Table 1| The ratio of the experimental kinetic energy K_{exp} extracted from optical measurements, as described in ref. 27, and K_{LDA} provided by band-structure calculations.

*D. van der Marel etal., unpublished; **A. Schafgans etal., unpublished.

Basov and Chubakov, Nature Physics 2011



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.

DFMT

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.

ω [eV]

Sum rule

f-sum rule:

$$\int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi n e^2}{2m_e} = \omega_p^2/8$$

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:
$$\int_0^W \sigma_1(\omega) d\omega = W_K = \frac{\pi e^2}{2N} \Sigma \nabla_{k_x}^2 \epsilon_k n_k$$

kinetic energy in the tight binding model

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

 $\sigma(\omega,T) = \frac{\omega_p^2}{4\pi} \frac{1}{M(\omega,T) - i\omega}$
 $= \frac{\omega_p^2}{4\pi} \frac{1}{1/\tau(\omega,T) - i\omega[1 + \lambda(\omega,T)]}$
 $= \frac{1}{4\pi} \frac{\omega_p^{*2}}{1/\tau^*(\omega,T) - i\omega}$
 $1/\tau(\omega,T)$: Frequency dependent scattering rate
 λ : Mass enhancement $m^* = m(1 + \lambda)$
 $1/\tau(\omega,T) = (\omega_p^2/4\pi) \operatorname{Re}[1/\sigma(\omega,T)]$
 $m^*/m = 1 + \lambda(\omega) = (\omega_p^2/4\pi\omega) \operatorname{Im}[1/\sigma(\omega,T)]$

e.g. Marginal Fermi Liquid model:

$$M(\omega,T) = 1/\tau(\omega,T) - i\omega\lambda(\omega,T) \qquad \text{Where } \mathbf{x} = \max(|\omega|,T),$$

$$= g^2 N^2(0) \left(\frac{\pi}{2} x + i\omega \ln \frac{x}{\omega_c}\right) \qquad \text{or } \mathbf{x} = (\omega^2 + \alpha(\pi T)^2)^{1/2}$$

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, Nature 427, 714 (2004)

The electron-boson (phonon) interaction

$$1/\tau(\omega) = \frac{2\pi}{\omega} \int_{0}^{\infty} d\Omega(\omega - \Omega) \alpha_{tr}^{2}(\Omega) F(\Omega)$$

T=0 K P.B.Allen 1971



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

S. V. Dordevic, et al. PRB 71, 104529 (2005)

Allen's formula for the scattering rate in the superconducting state

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

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 $1/\tau_{cal}(\omega)$ from Eq. (13). For $\Delta=0$ the calculated scattering rate resembles $1/\tau(\omega)$ of underdoped YBa₂Cu₃O_{6.60} (Fig. 7). However, for finite values of the gap the calculated scattering rate resembles $1/\tau(\omega)$ of optimally doped YBa₂Cu₃O_{6.95}: there is an *overshoot* following the suppressed region (Fig. 7).

Optical spectra of a superconductor

T=0, London electrodynamics gives

$$\sigma = \frac{1}{8} \omega_{ps}^{2} \delta(\omega) + i \omega_{ps}^{2} / 4\pi \omega \implies \frac{1}{\lambda_{L}^{2}} = \frac{8}{c^{2}} \int_{0}^{\infty} (\sigma_{1}^{n} - \sigma_{1}^{s}) d\omega \quad \text{or} \quad \frac{1}{\lambda_{L}^{2}} = \frac{4\pi}{c^{2}} \omega \sigma_{2}(\omega)$$
Ferrell-Glover-Tinkham sum-rule: missing area
is equal to the superconducting condensate.
Clean limit $\exists \xi = 1 \iff 2\Delta < \Gamma$
Absorption starts at 2Δ .
Clean limit: $\xi < 1 \iff 2\Delta > \Gamma$
Absorption starts at $2\Delta + \Omega$.
$$\vdots$$
 pippard coherence length
 $\xi = v_{F}/\pi\Delta, \Gamma = 1/\tau = v_{F}/I$

Coherent factors and characteristic spectral structures in density wave or superconductors

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

P



$$\frac{\sigma_1^S}{\sigma_1^N} = \frac{1}{\hbar\omega} \int\limits_{-\infty}^{\infty} \frac{\left|E(E+\hbar\omega)\mp\Delta^2\right|}{(E^2-\Delta^2)^{1/2}[(E+\hbar\omega)^2-\Delta^2]^{1/2}} [f(E) - f(E+\hbar\omega)] dE$$

Gap feature in density waves

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PHYSICAL REVIEW LETTERS

13 May 1996

Direct Observation of the Spin-Density-Wave Gap in (TMTSF)₂PF₆

L. Degiorgi Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

M. Dressel,* A. Schwartz, B. Alavi, and G. Grüner Department of Physics, University of California, Los Angeles, California 90095-1547





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



Gap structure in superconductors

Ba_{0.6}K_{0.4}Fe₂As₂



G. Li et al PRL 08



Cuprates, Homes data

Coherent peak below Tc



O.Klein et al PRB 94

铁基超导体的THz数据与NMR不同? S+-配对?



Optical measurement under magnetic field





Effect of magnetic field:



Magneto-Optical Reflectivity in EuB6

Degiorgi et al., Phys. Rev. Lett. 79, 5134 (1997)

Pump-probe experiment based on femtosecond laser







THz time domain spectroscopy







Optical (e.g. midinfrared) pump, THz probe !

Manipulation and control



Femtosecond laser can **selectively excite certain modes** of correlated electronic systems, and controllably push materials from one ordered phase to another.



Light-Induced Superconductivity in a Stripe-Ordered Cuprate

Science 2011

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dots) and below (red dots) $T_c = 38$ K. Here field reflectances $r = E_{refl}/E_{inc}$ are measured, as opposed to intensity reflectivities in the near-IR, because the time domain detection scheme for short terahertz transients is sensitive to the electric field.

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 LESCO_{1/8} at 10 K. The optical properties are those of a nonsuperconducting compound down to the lowest temperatures. (**C**) Transient *c*-axis reflectance of LESCO_{1/8}, normalized to the static reflectance. Measurements are taken at 10 K, after excitation with IR pulses at 16 μ m wavelength. The appearance of a plasma edge at 60 cm⁻¹ demonstrates that the photoinduced state is superconducting.

Frequency (cm⁻¹)

Thanks!