Optical study on CuxTiSe2

N. L. Wang

Institute of Physics, CAS

Collaborators

G. Li, W. Z. Hu

Institute of Physics, CAS

D. Qian, D. Hsieh, Z. Hasan

Department of Physics,
Princeton University

E. Morosan, R. J. Cava

Department of Chemistry,
Priceton University

ARPES

CuxTiSe2 crystals

Outline

- Structure in dichalcogenides

  1 T and 2 H phases

- Coexistence and competition between CDW and SC

- Parent compound 1T-$TiSe_2$

  semimetal or semiconductor?

  mechanism of CDW transition:

  excitonic or others

- Cu-doped compound Cu_xTiSe_2

  evolution

  x=0.07, anomalous metallic state

2H structure

a=3.314 A, c=12.090 A

Space group *P*6/mmc

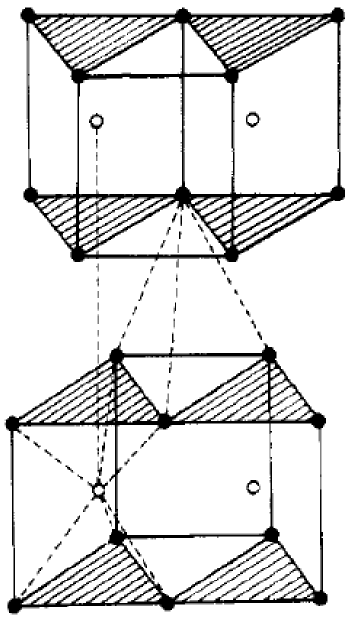


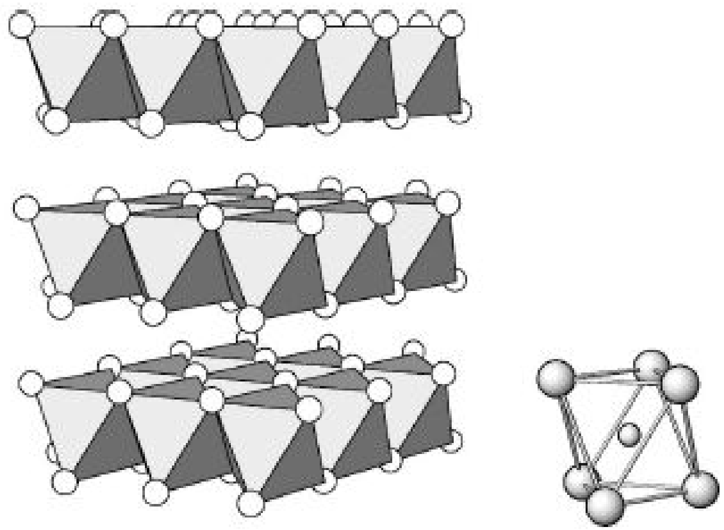
Figure 1. Structure of the 2H-metallic transition-metal dichalcogenides; ● chalcogens, ○ metals.

2H-TaS_2

1T structure

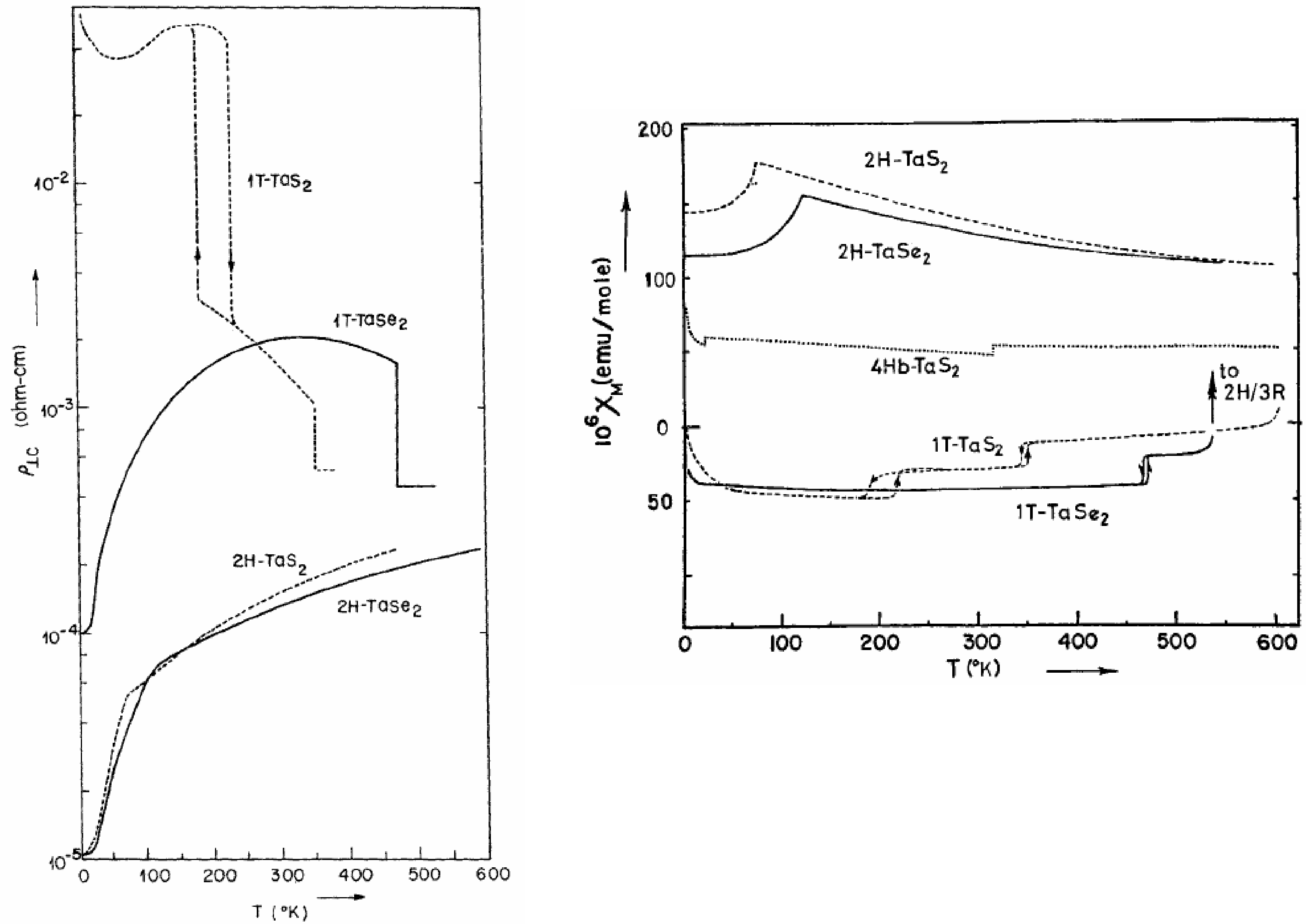
A=3.364 A c=5.897 A

Space group: *P*3m1



1T-TaS_2

Fig. 3


1T-TaS2
1T-TaSe2
2H-TaS2
2H-TaSe2
ρ⊥c (ohm-cm)
10-2
10-3
10-4
10-5
0 100 200 300 400 500 600
T (°K)
2H-TaS2
2H-TaSe2
4Hb-TaS2
to 2H/3R
1T-TaS2
1T-TaSe2
10^6 χM (emu/mole)
200
100
0
50
T (°K)

Coexistence and competition between CDW and SC:

	2H-TaSe2,	2H-TaS2,	2H-NbSe2,	2H-NbS2
T_{CDW}:	122 K (90 K),	75 K,	35 K,	0 K
T_{sc}:	0.14 K,	0.7 K,	7.2 K,	6 K

Na-intercalated 2H-TaS2:

CDW suppressed, but SC increases

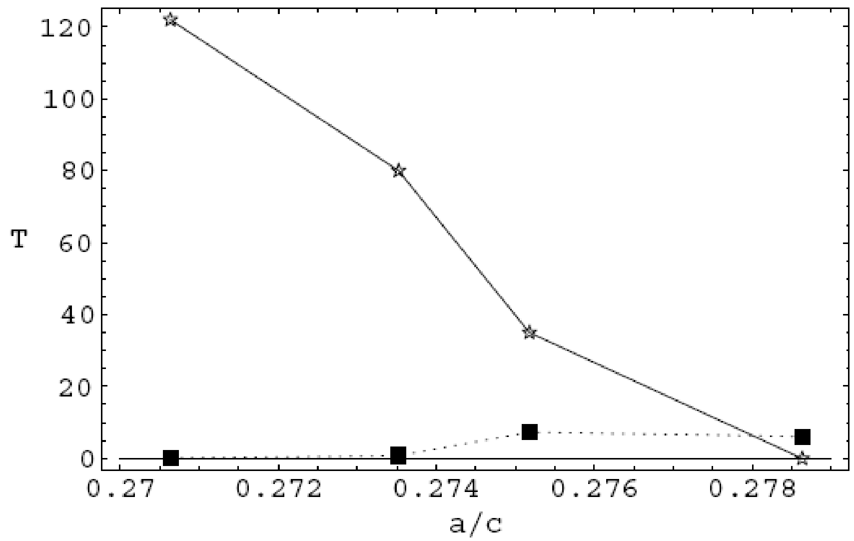


FIG. 1. Phase diagram: Stars, T_{CDW}; filled squares, T_c. From left to right: $TaSe_2$, TaS_2, $NbSe_2$, and NbS_2 [2,3]. a is the in-plane lattice spacing and c is the interlayer spacing.

A. H. Castro Neto, PRL (01)

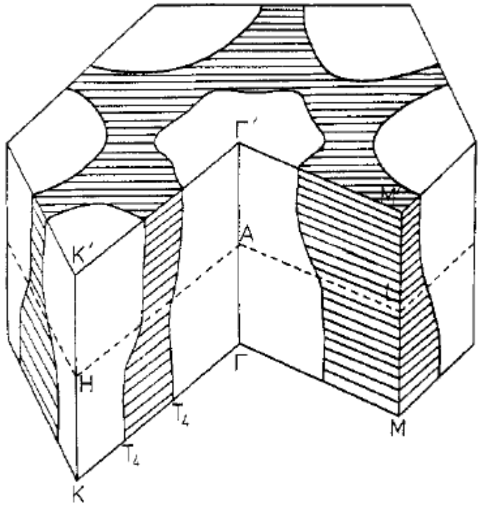
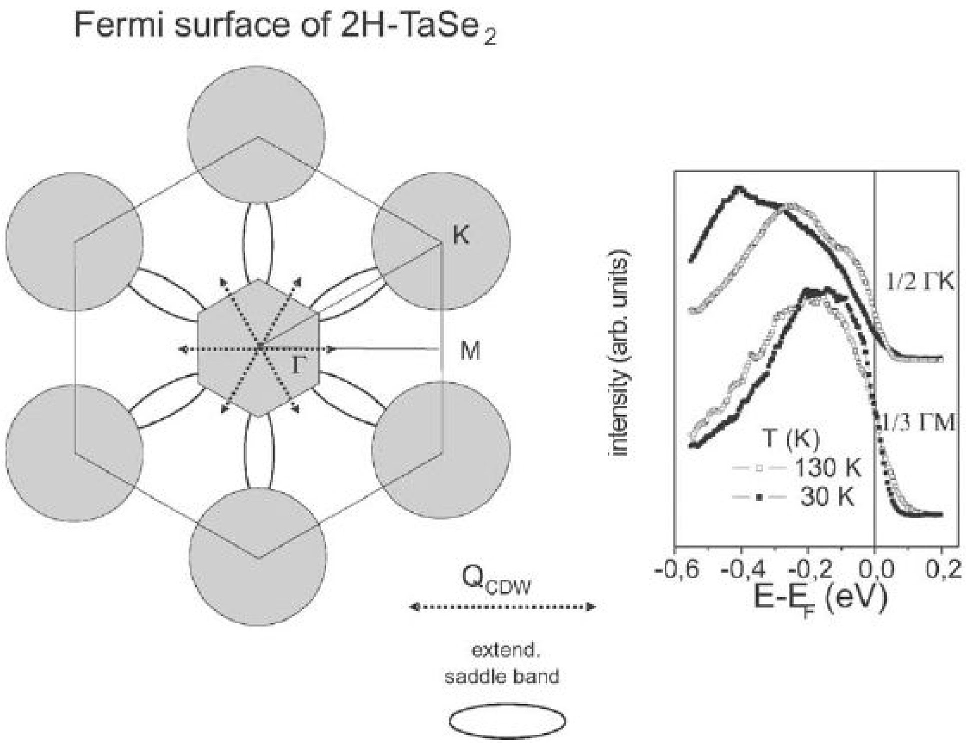


Figure 2. Schematic representation of the Fermi surface of $2H\text{-}NbSe_2$ unfolded into the double Brillouin zone.

O. Seifarth et al. / Journal of Electron Spectroscopy and Related Phenomena 137–140 (2004) 675–679



CDW wave vector is 1/3**b** (2/3Γ**M**) regardless of doping, or element.

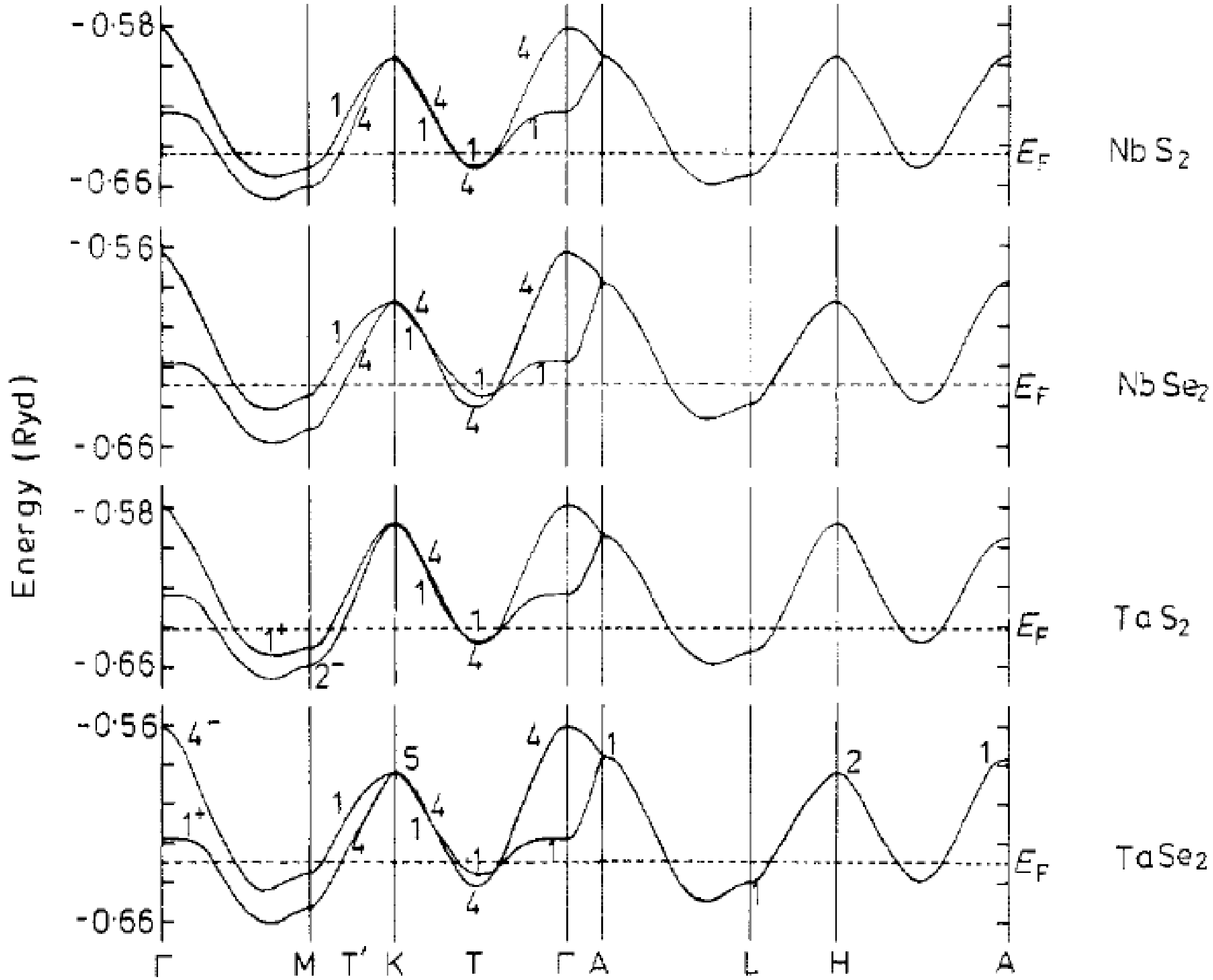


Figure 4. Lowest d sub-band (d_{z^2} at Γ) for the four 2H-VB dichalcogenides. The small differences between the Nb and Ta compounds may be increased by relativistic corrections.

Fermi surfaces and band structures of the 2H metallic transition-metal dichalcogenides

G Wexler and A M Woolley
Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, England

Received 8 August 1975

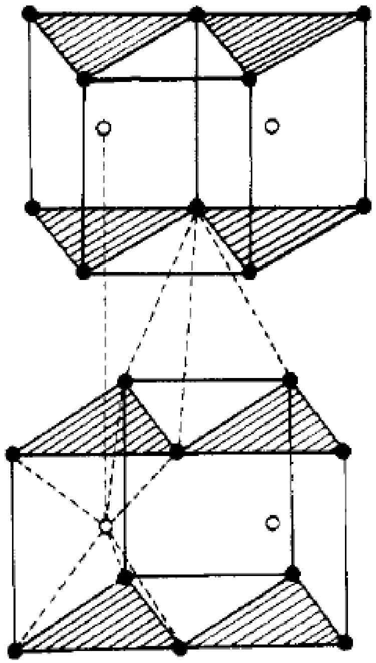
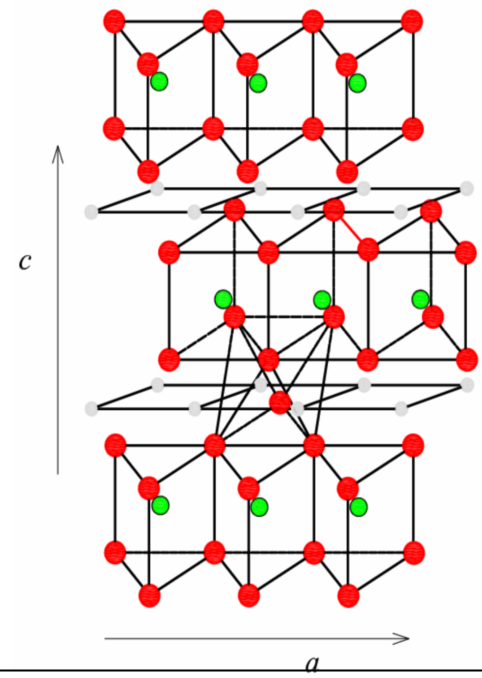


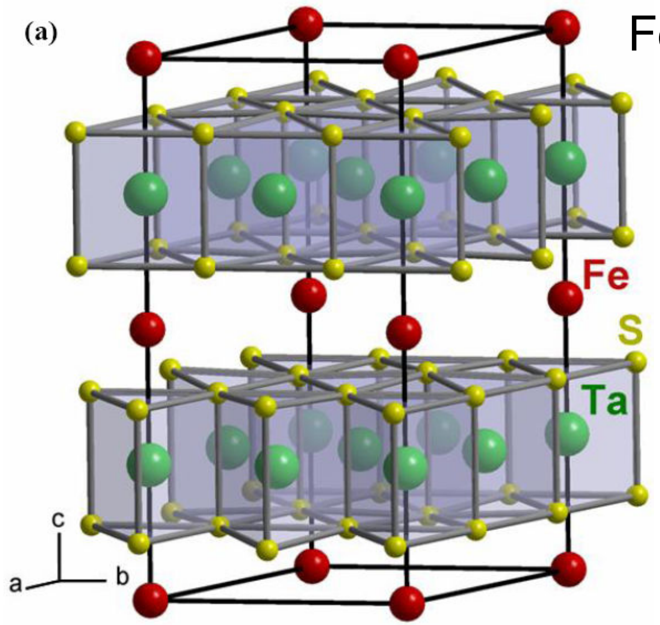
Figure 1. Structure of the 2H-metallic transition-metal dichalcogenides; ● chalcogens, ○ metals.

插层



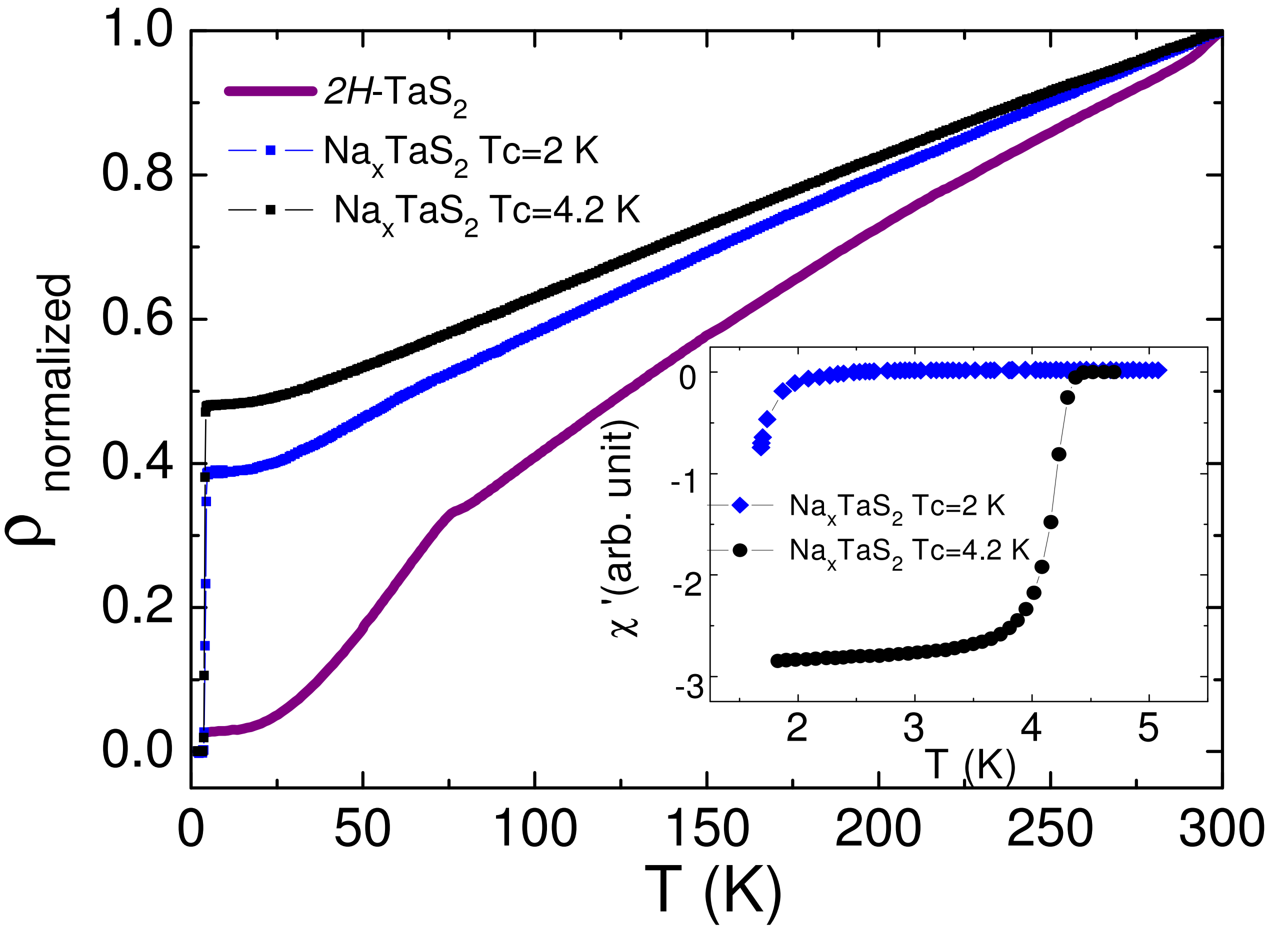
LixNbO2

Fe1/4TaS2



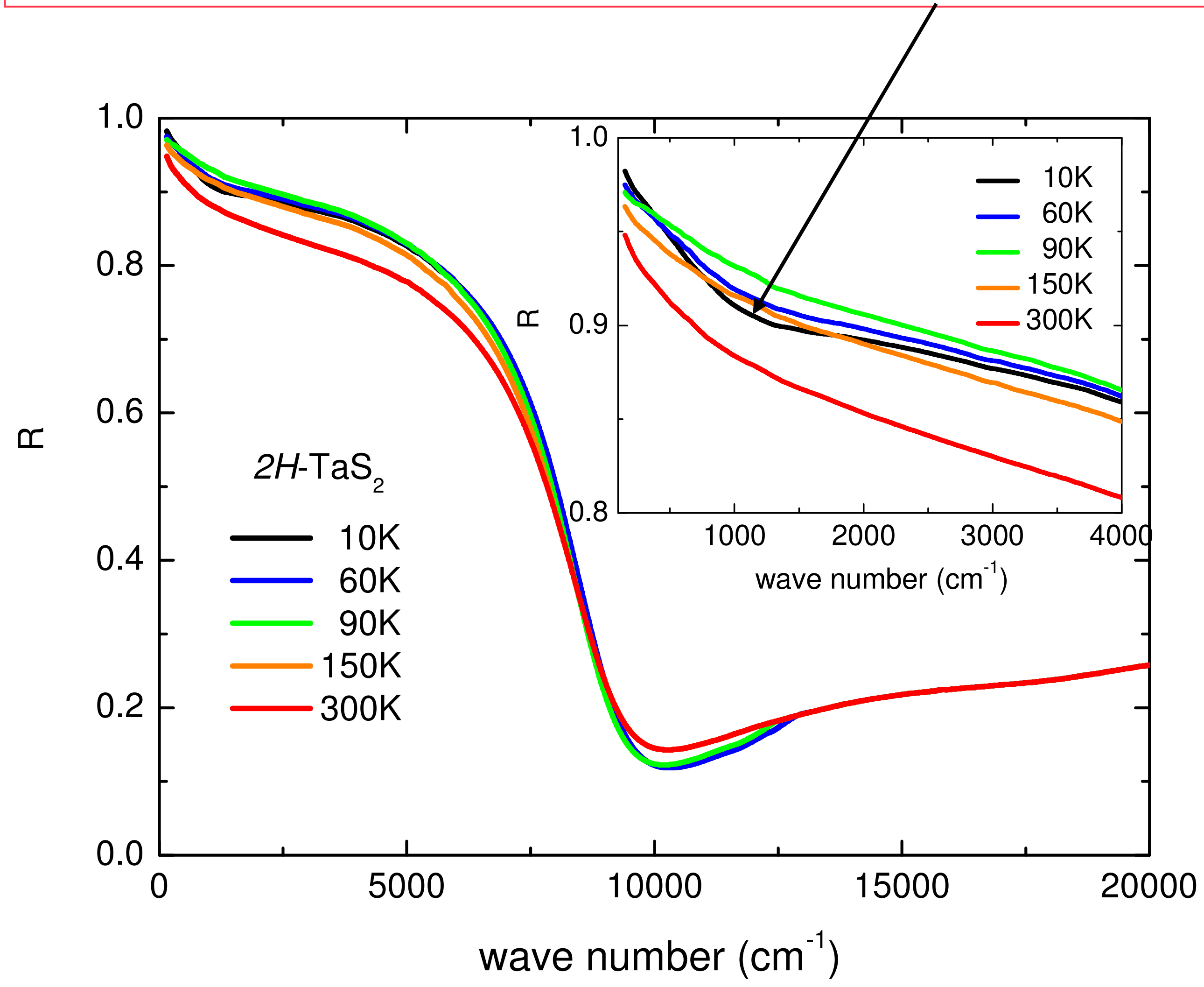
E. Morosan et al. cond-mat/0701311

2H-NaxTaS2



2H-TaS2
NaxTaS2 Tc=2 K
NaxTaS2 Tc=4.2 K
ρ normalized
T (K)
χ '(arb. unit)

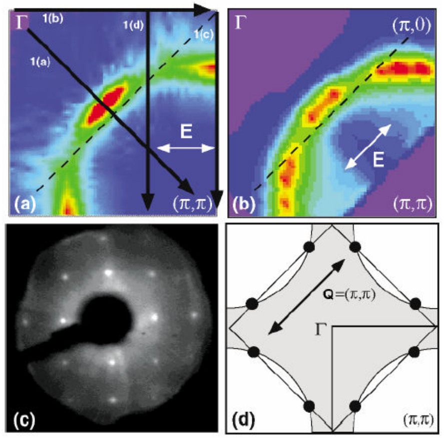
Typical behavior of partial energy gap at Fermi surface in R(ω)

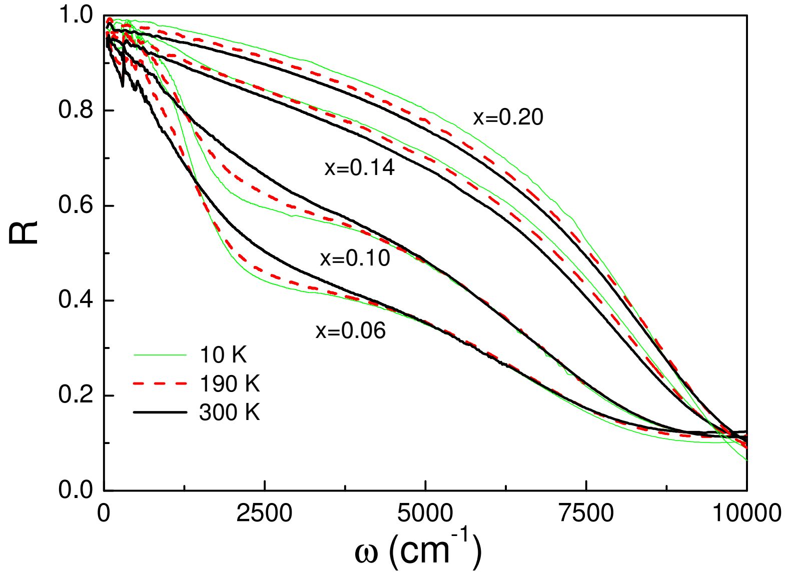


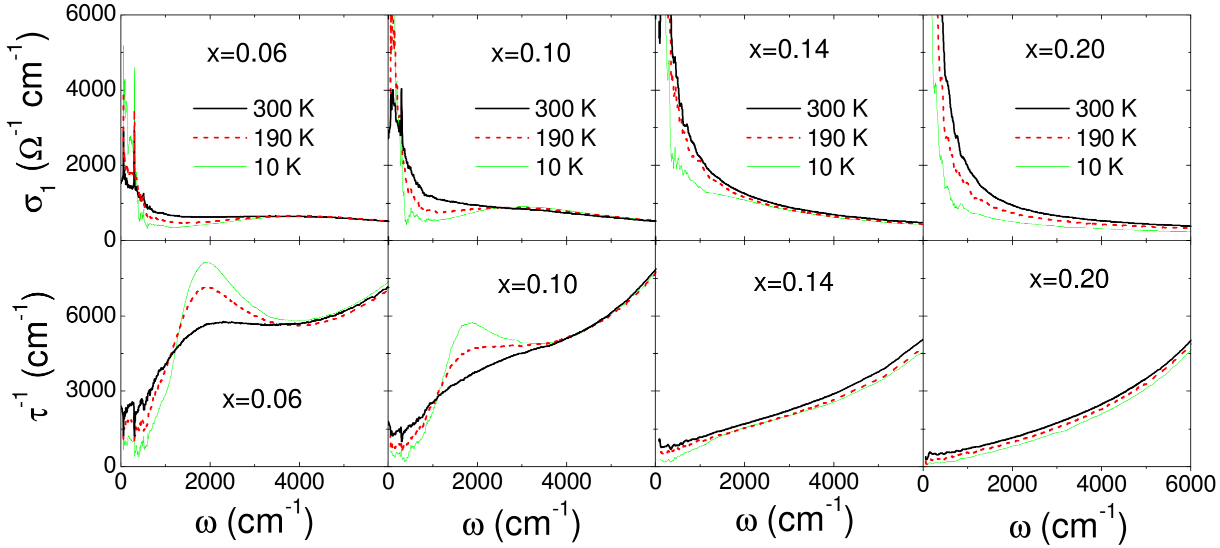
W. Z. Hu et al., con-mat/0703166

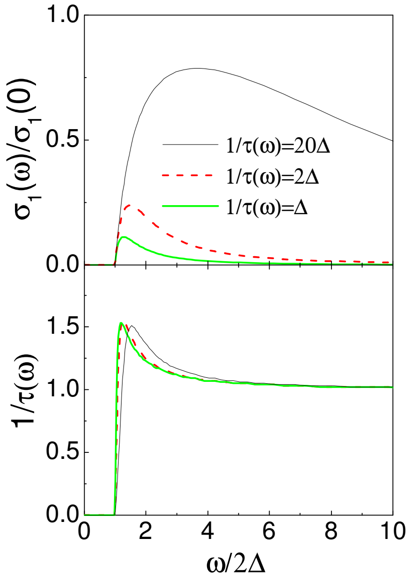
Nd2-xCexCuO4

NL Wang et al. PRB 06



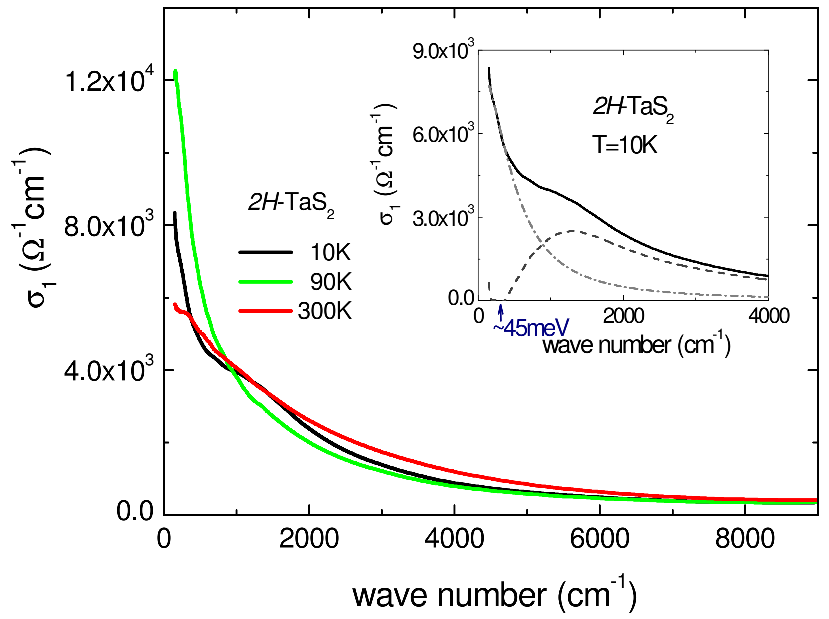


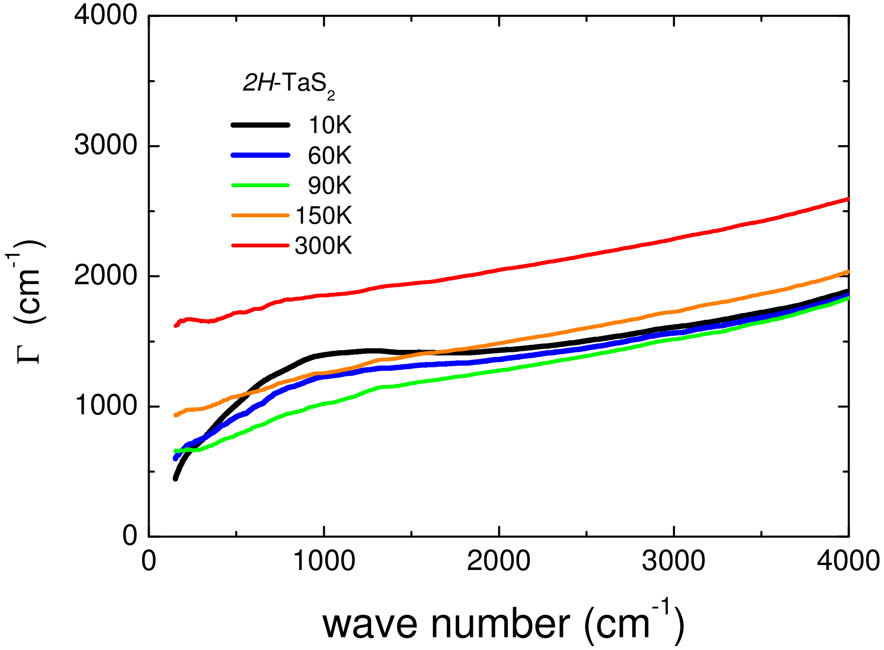


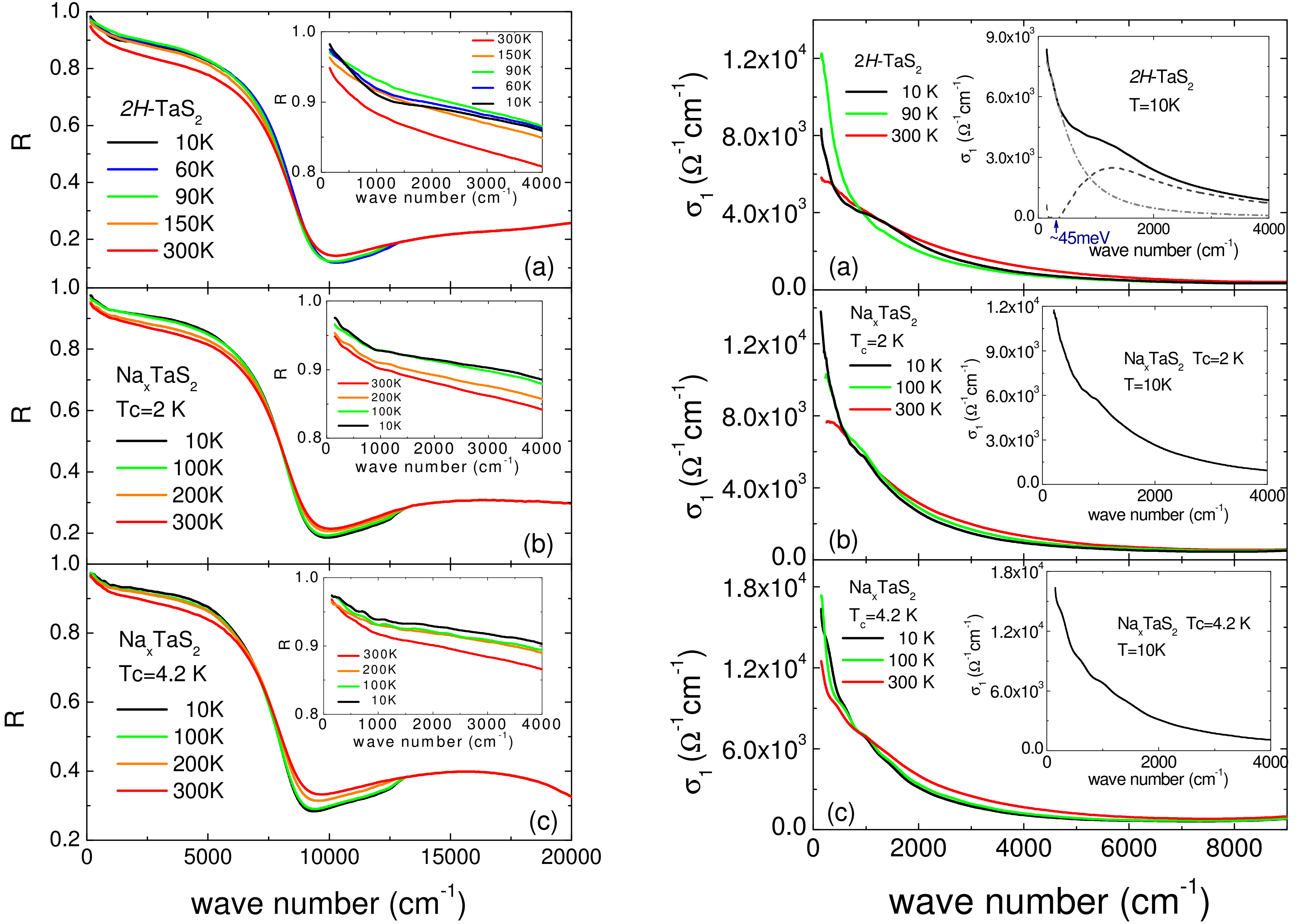


BCS s-wave gap

$$\Gamma(\omega) = \frac{1}{\tau(\omega)} = \frac{\omega_p^2}{4\pi}\mathrm{Re}\left(\frac{1}{\sigma(\omega)}\right)$$

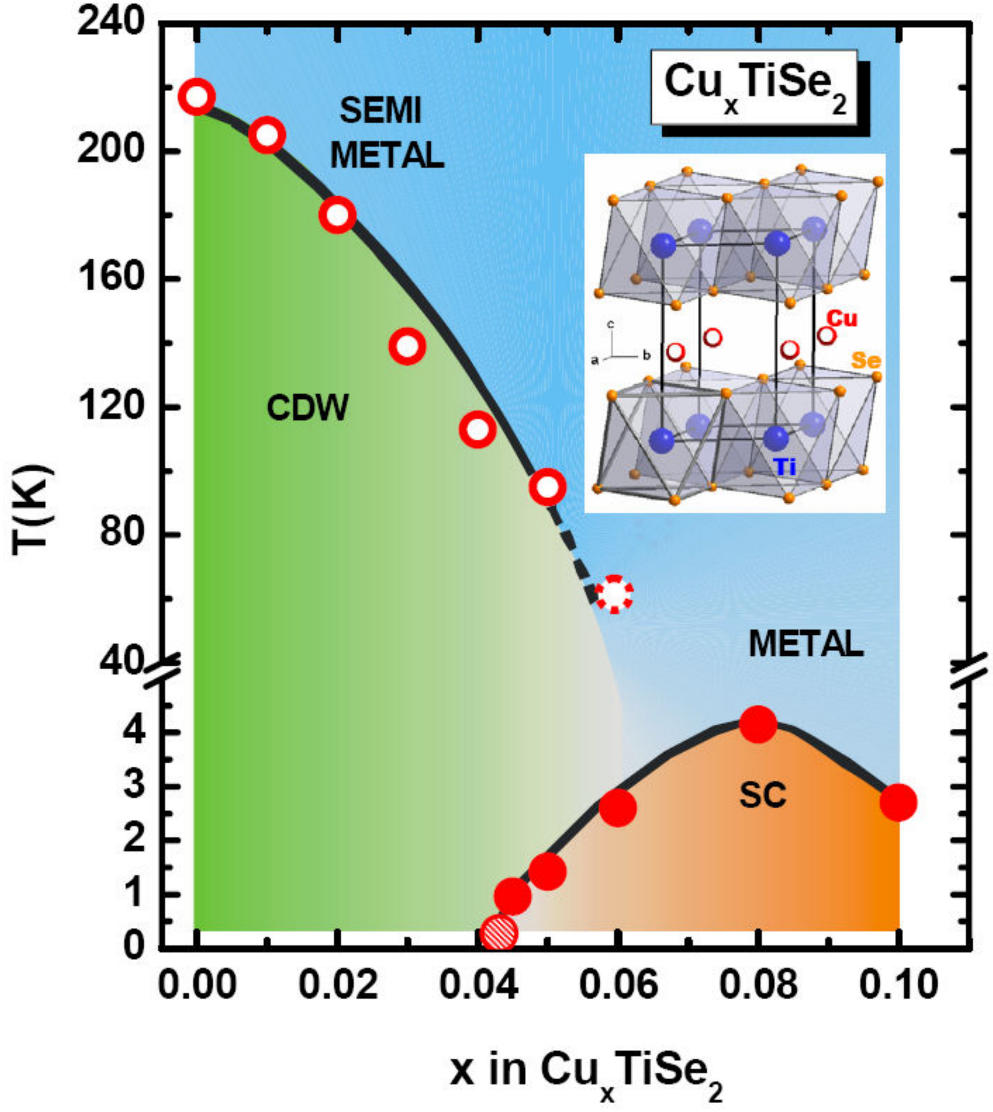


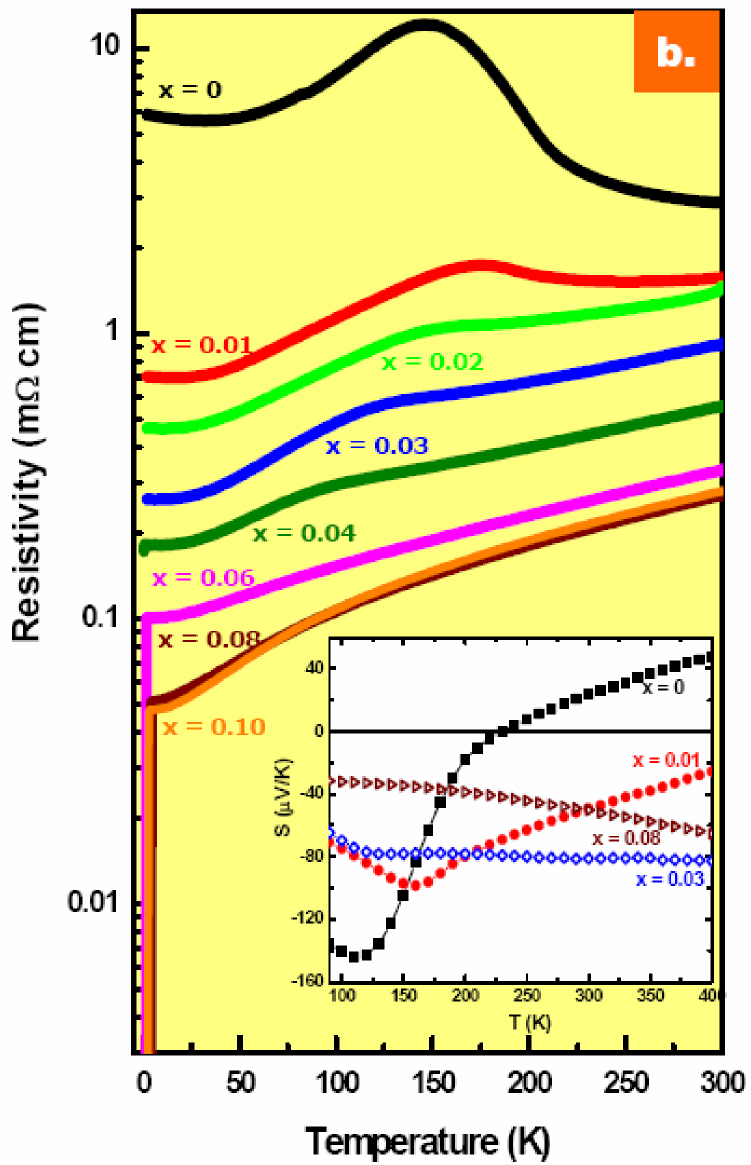




R
2H-TaS2
10K
60K
90K
150K
300K
(a)
Na_xTaS_2
Tc=2 K
10K
100K
200K
300K
(b)
Tc=4.2 K
(c)
wave number (cm-1)
σ1 (Ω-1cm-1)
10 K
90 K
300 K
T=10K
~45meV
Tc=2 K
100 K
Tc=4.2 K

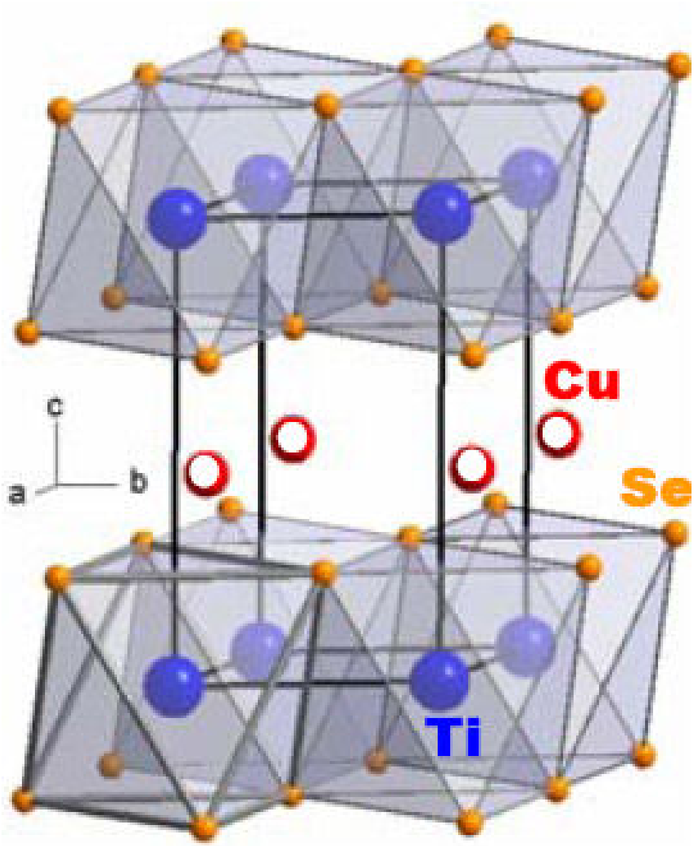
Newly discovered Cu_xTiSe_2





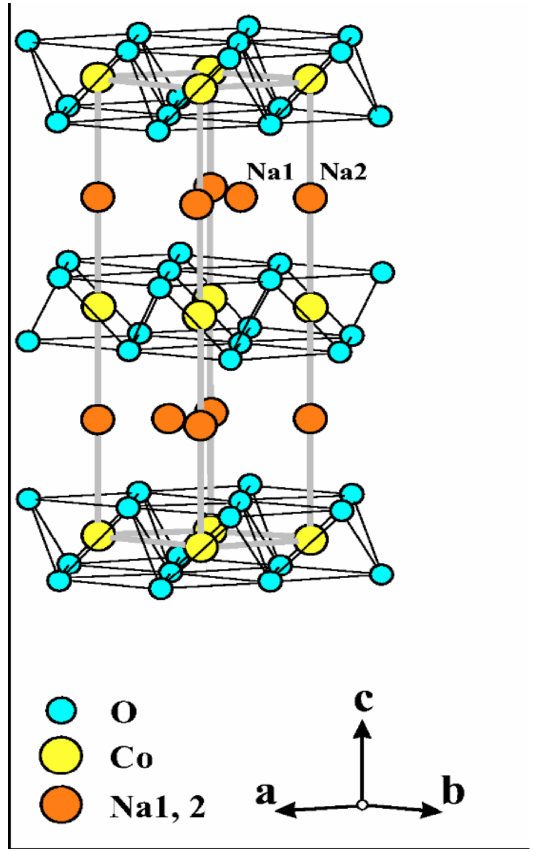
Cava group, Nature Phys. 06

Only superconductor with 1T structure



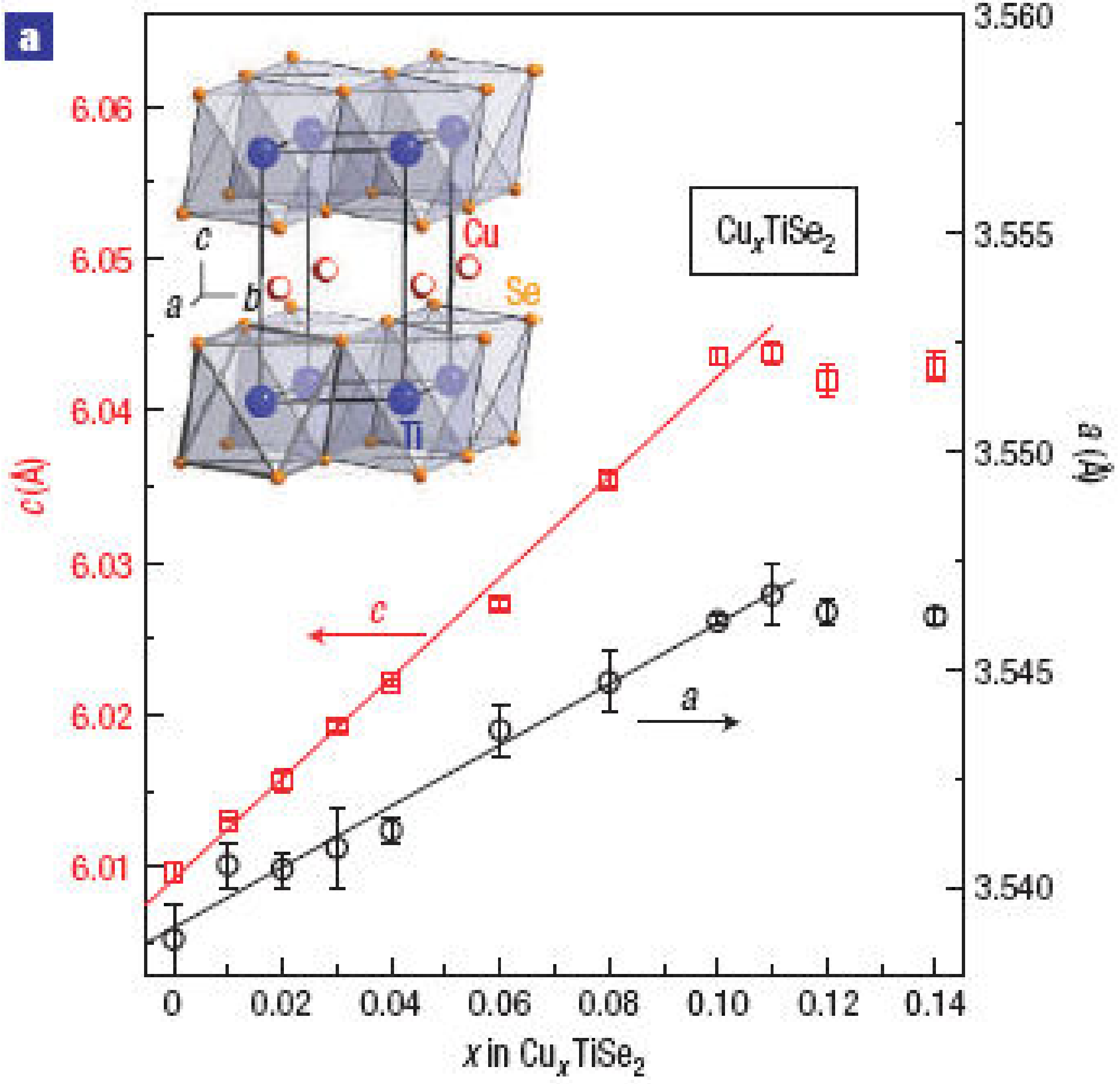
Na_xCoO_2

a=2.84 A c=10.81 A,
space group: P6/mmc



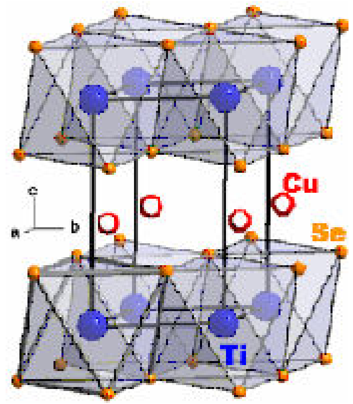
2H + 1T structural block

Lattice parameter with x, space group $P\bar{3}m1$

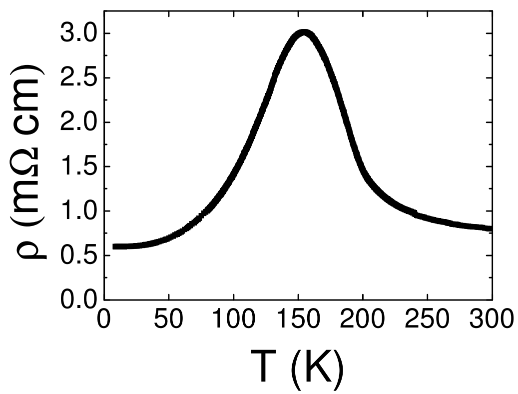


Parent compound 1T-TiSe2

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



- Broken symmetry at 200 K with a 2x2x2 superlattice



PHYSICAL REVIEW B VOLUME 17, NUMBER 4 15 FEBRUARY 1978

Band structure and lattice instability of $TiSe_2$

Alex Zunger*
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, Illinois 60201

A. J. Freeman
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, Illinois 60201 and Argonne National Laboratory, Argonne, Illinois 60439

(Received 23 June 1977)

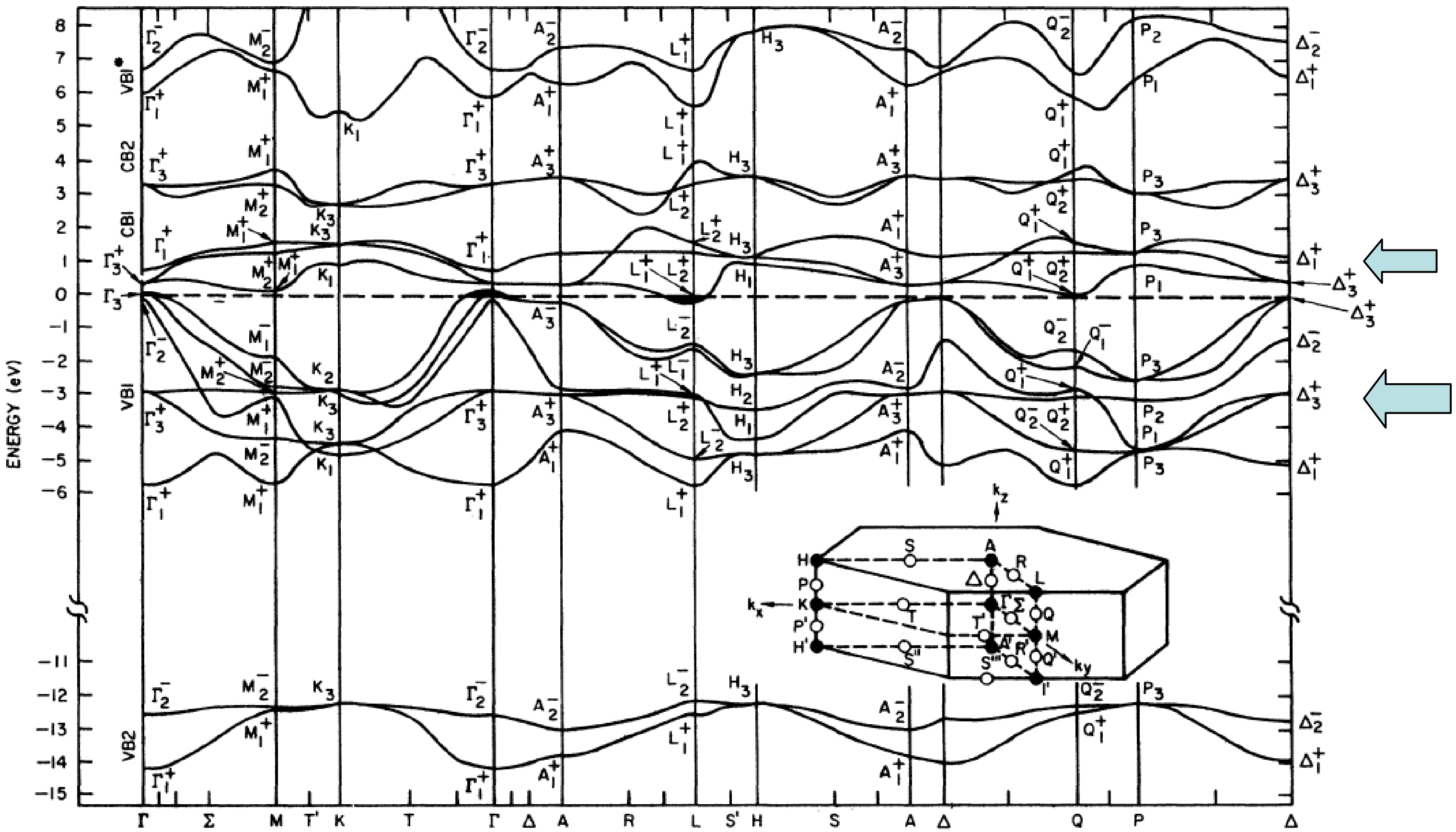


FIG. 1. Energy-band structure of $TiSe_2$ in the local exchange and correlation model.

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

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

Ti : 3d band

Se: 4p band

Emergence of Fermi Pockets in a New Excitonic Charge-Density-Wave Melted Superconductor

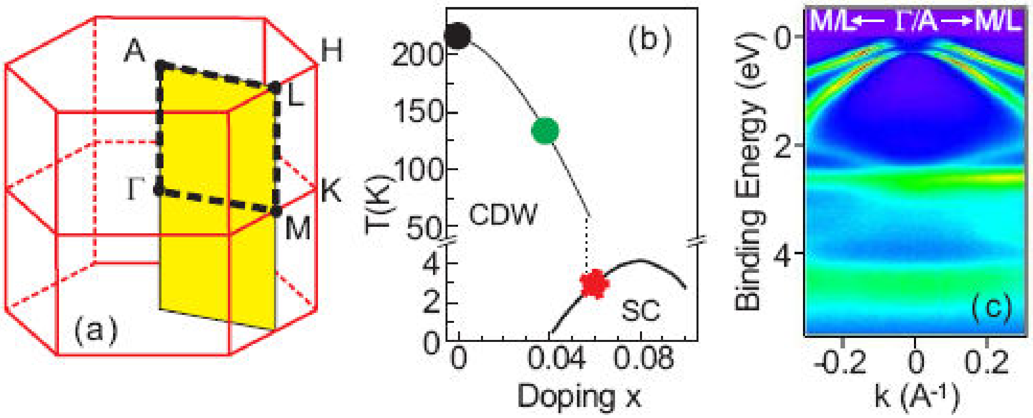
D. Qian,[1] D. Hsieh,[1] L. Wray,[1] E. Morosan,[2] N. L. Wang,[3] Y. Xia,[1] R. J. Cava,[2] and M. Z. Hasan[1,4,*]

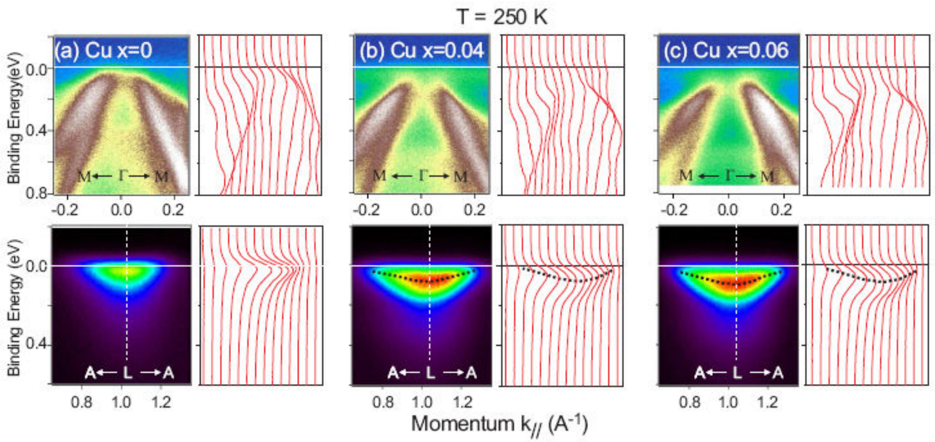
[1]*Department of Physics, Joseph Henry Laboratories of Physics, Princeton University, Princeton, New Jersey 08544, USA*

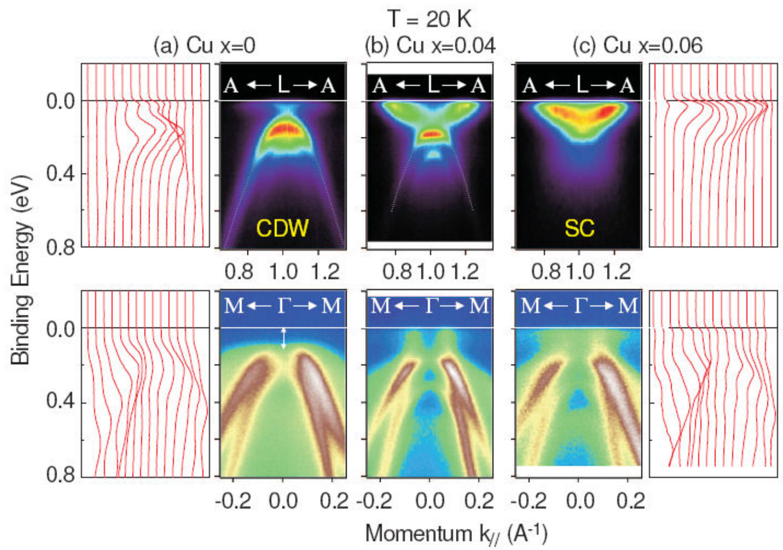
[2]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

[3]*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

[4]*Princeton Center for Complex Materials, School of Engineering, Princeton University, Princeton, New Jersey 08544, USA*



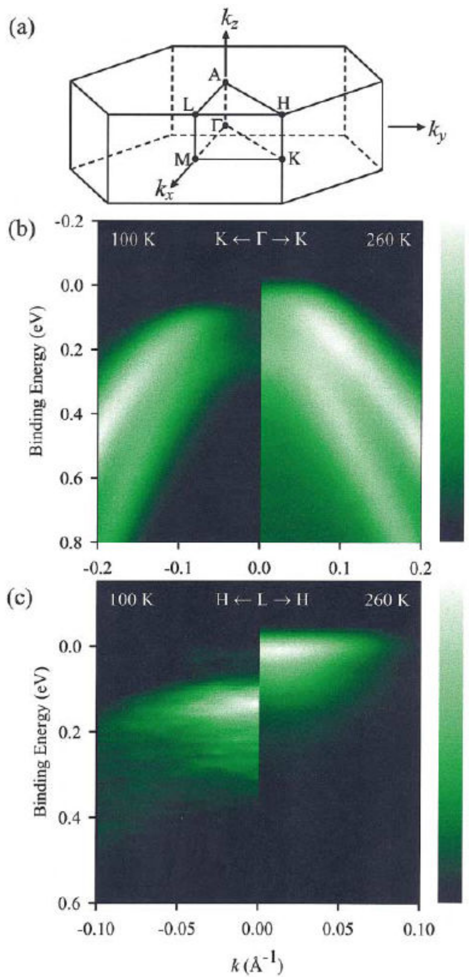


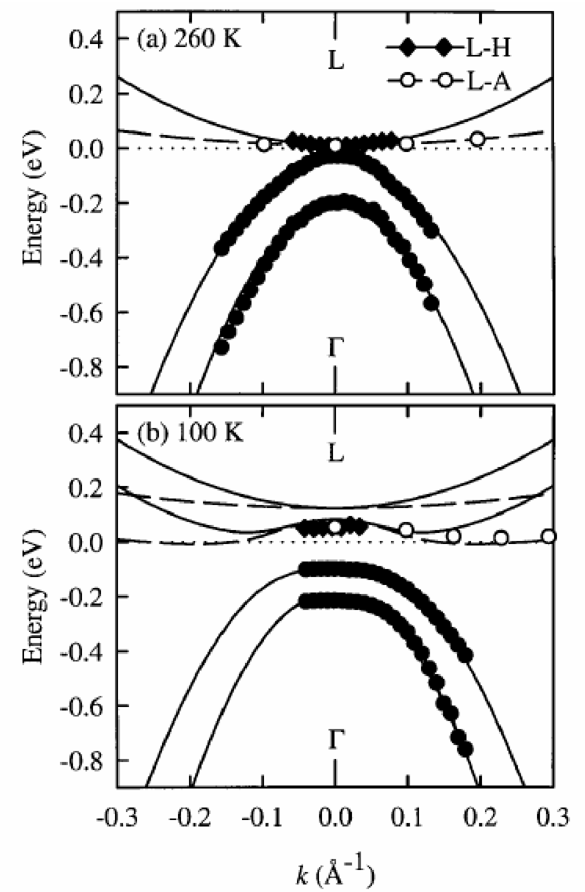


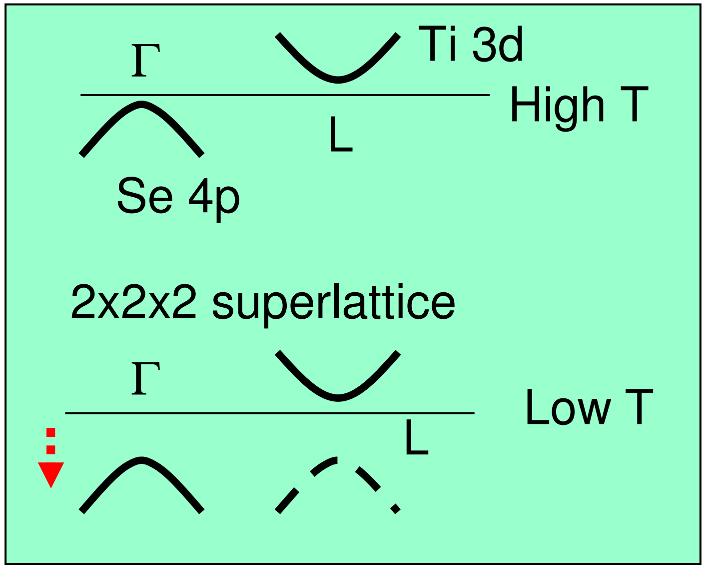
VOLUME 88, NUMBER 22 PHYSICAL REVIEW LETTERS 3 JUNE 2002

Electron-Hole Coupling and the Charge Density Wave Transition in $TiSe_2$

T. E. Kidd,[1] T. Miller,[1] M. Y. Chou,[2] and T.-C. Chiang[1,*]
[1]*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080*
and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801-2902
[2]*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430*
(Received 8 November 2001; published 17 May 2002)





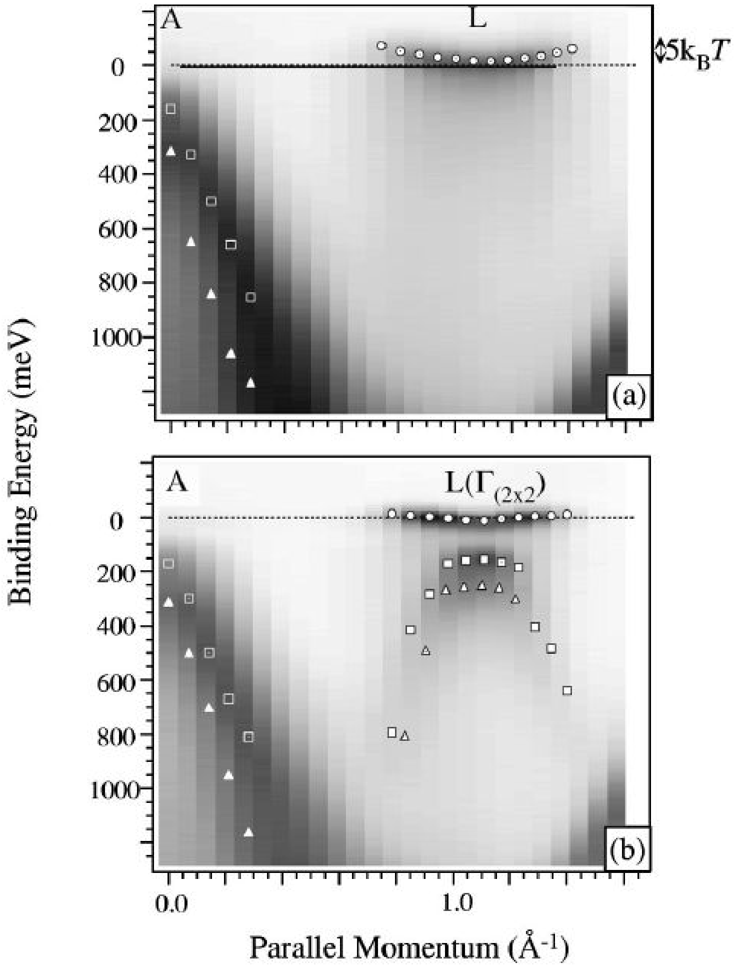


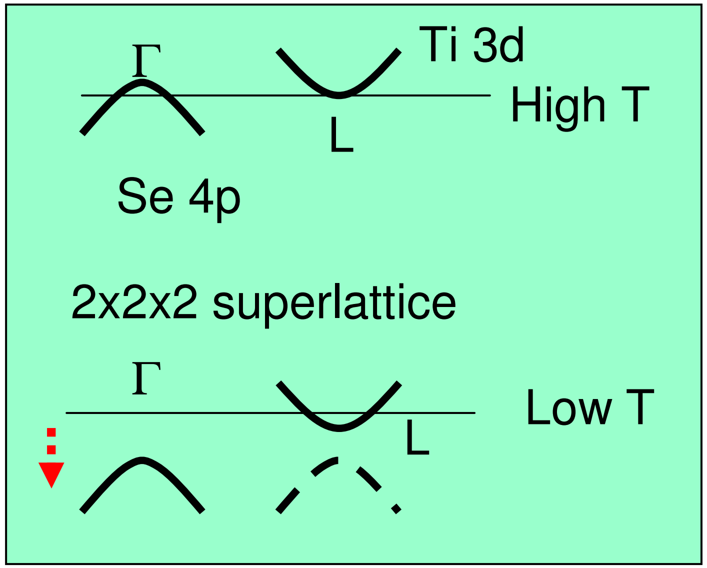
No band crossing
Fermi level below CDW.

It is insulating!!

Photoemission of bands above the Fermi level: The excitonic insulator phase transition in 1T-$TiSe_2$

Th. Pillo, et al. PRB (2000)





metallic picture

But does not satisfy the charge neutrality!! X

Issue

- ARPES experiments did not resolve conclusively whether the compound is a semimetal or semiconductor with a small indirect gap.

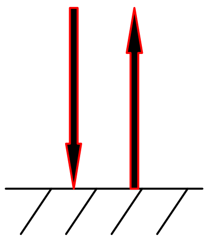
- The mechanism of the CDW transition:

  not due to the Fermi Surface nesting or saddle-point singularity

Optical measurement

Experiment:

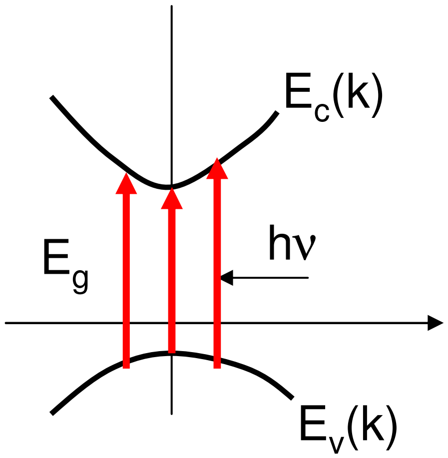
Reflectivity R(ω)



Interband transition

$|v,k>, E_v(k)$

$|c,k>, E_c(k)$



$$\hbar\omega = E_c(k) - E_v(k) \equiv E_{cv}(k)$$

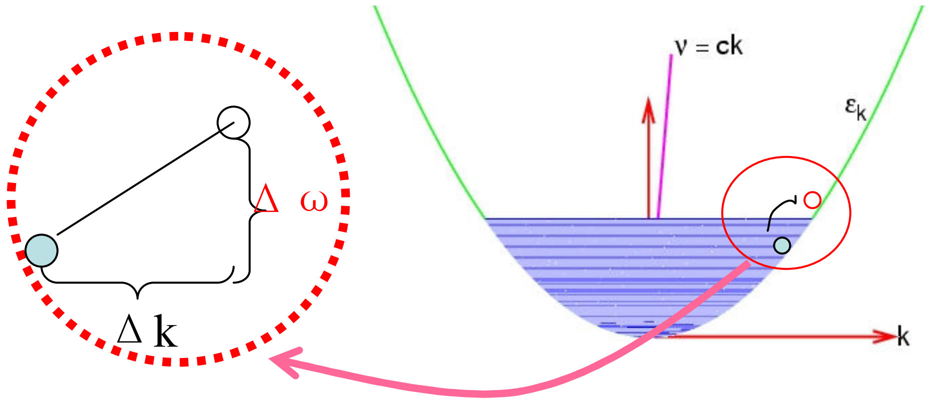
$$J(E) = \frac{V}{(2\pi)^3}\int \frac{ds}{|\nabla_k E_{cv}(k)|}$$

Kubo-Greenwood formula

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{m^2\omega^2} J(\hbar\omega)|\vec{p}_{vc}(\hbar\omega)|^2$$

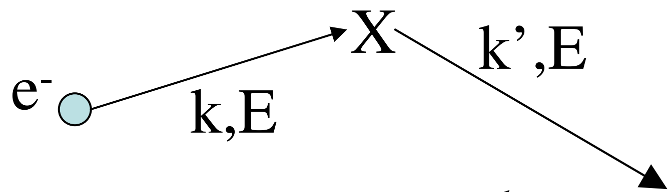
$$\sigma_1(\omega) = \frac{1}{4\pi}\omega\varepsilon_2(\omega)$$

Intraband transition

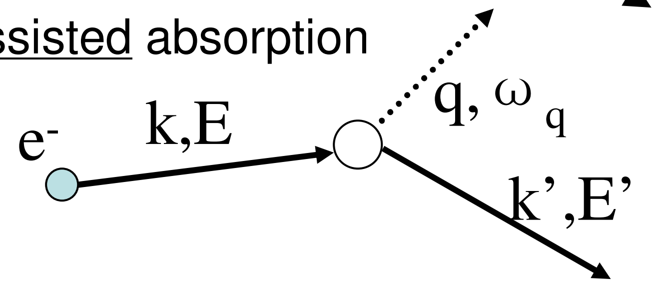


Infrared light cannot be absorbed directly by electron-hole excitation.

(a) Impurity-assisted absorption



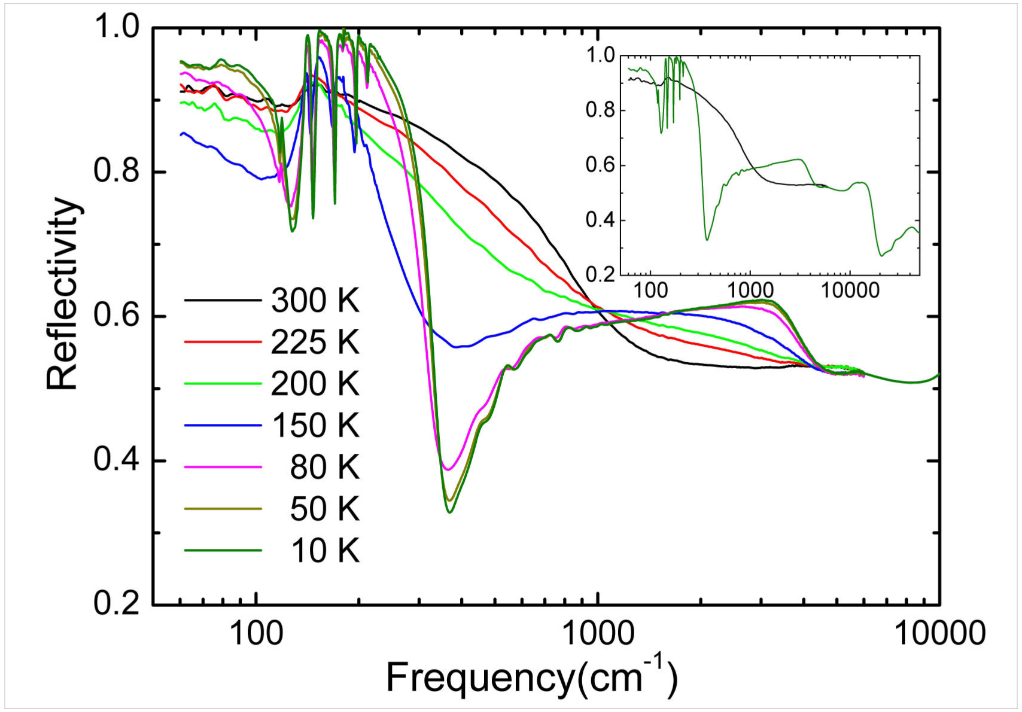
(b) boson-assisted absorption

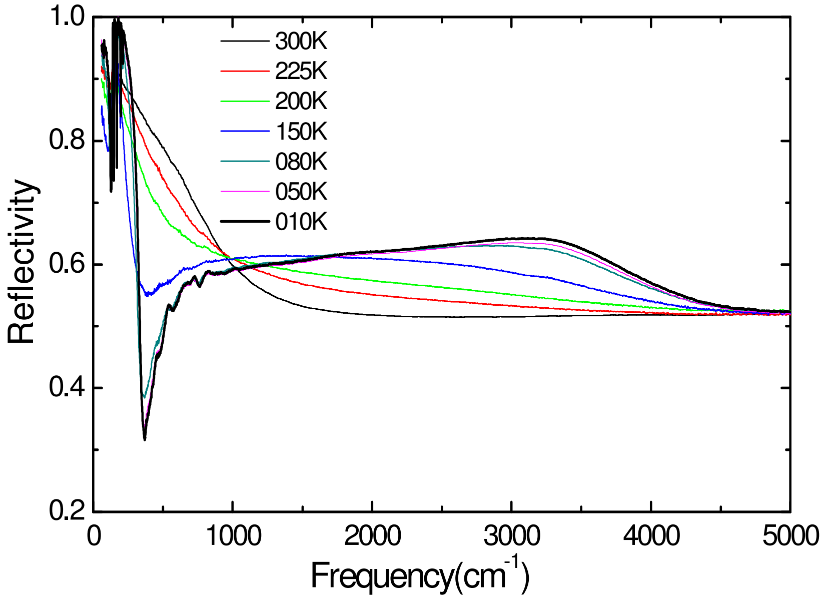


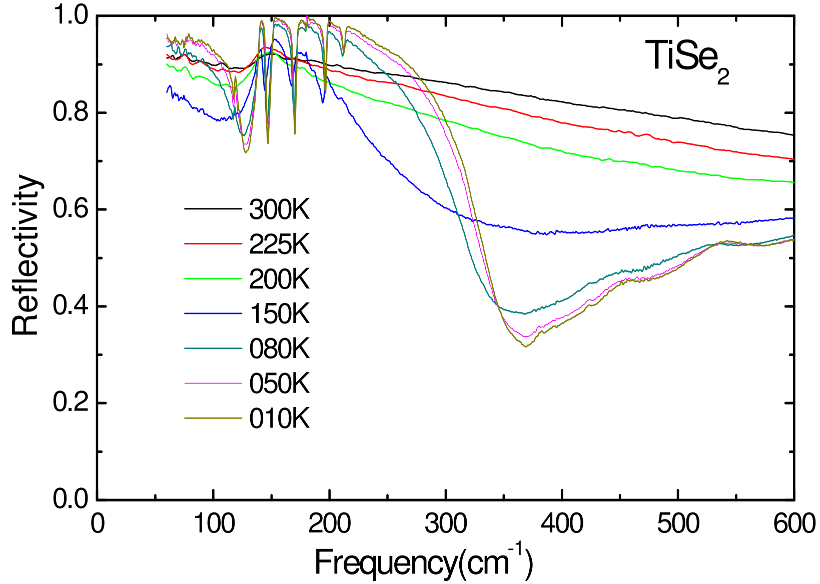
Holstein process, if phonons are involved.

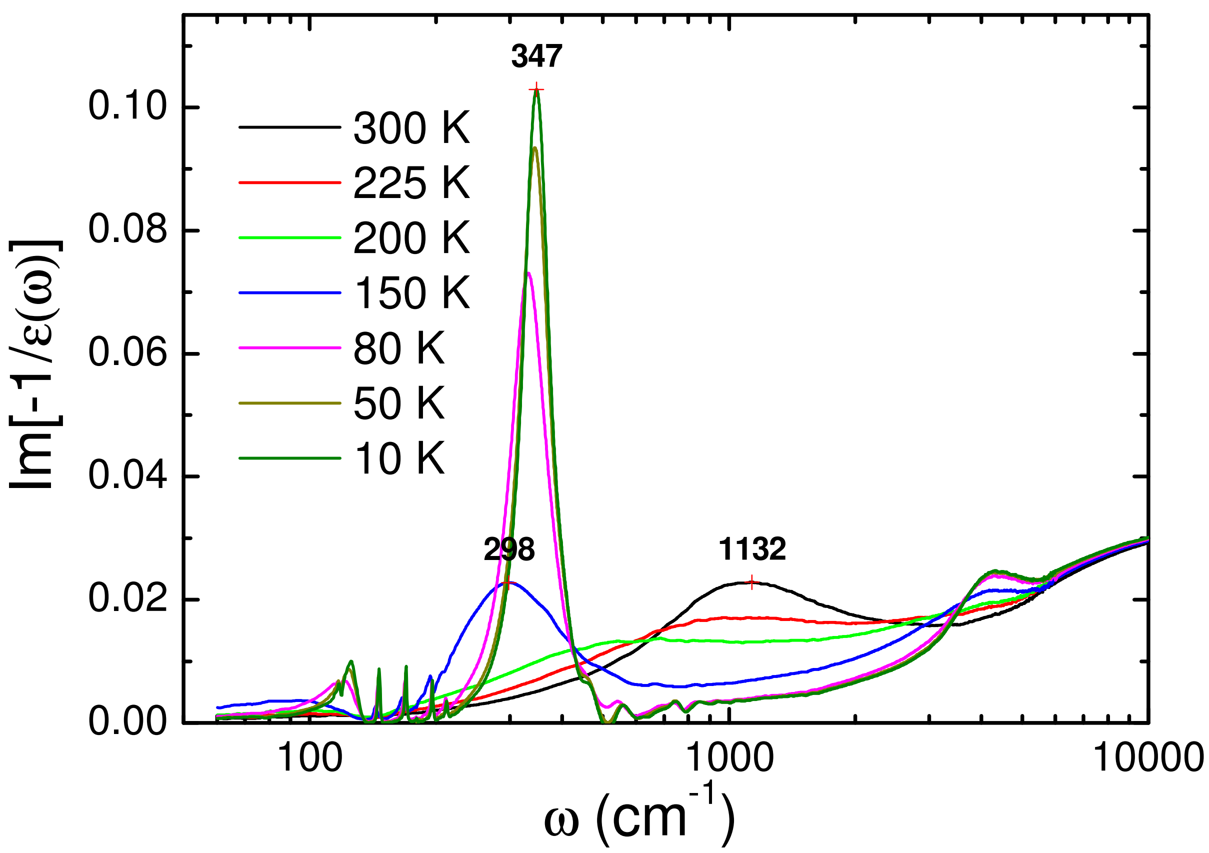
$TiSe_2$ single crystal

G. Li et al., cond-mat/0703167

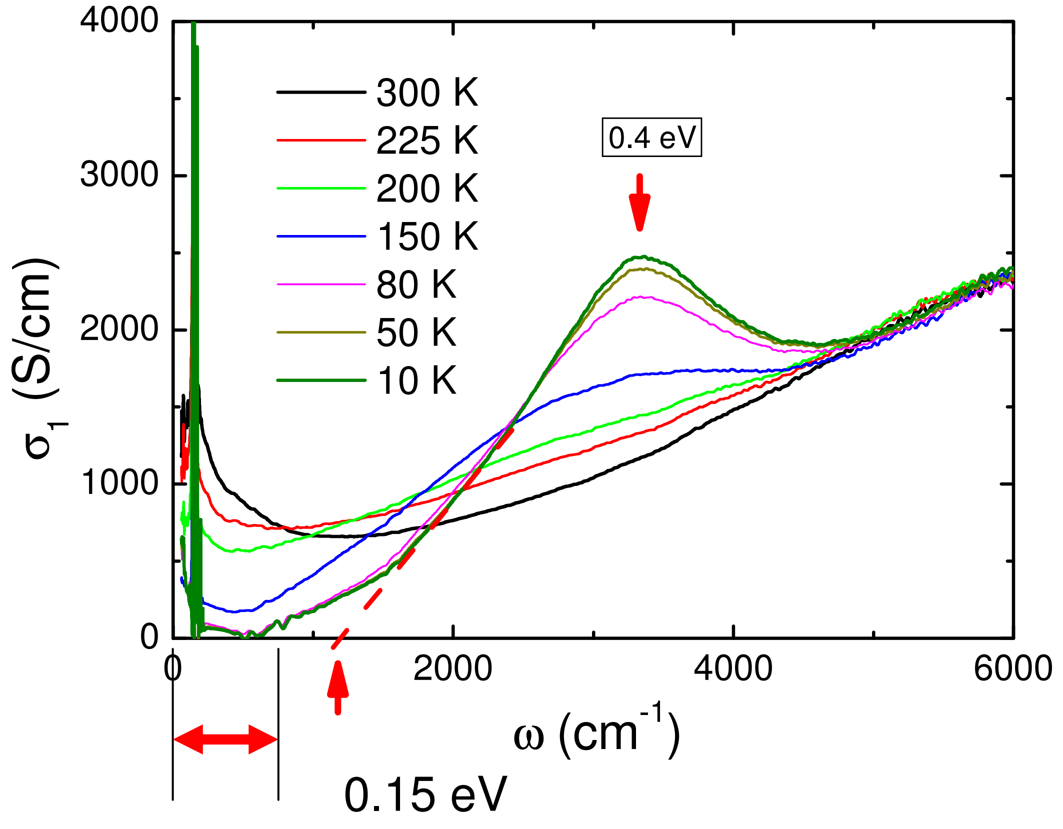






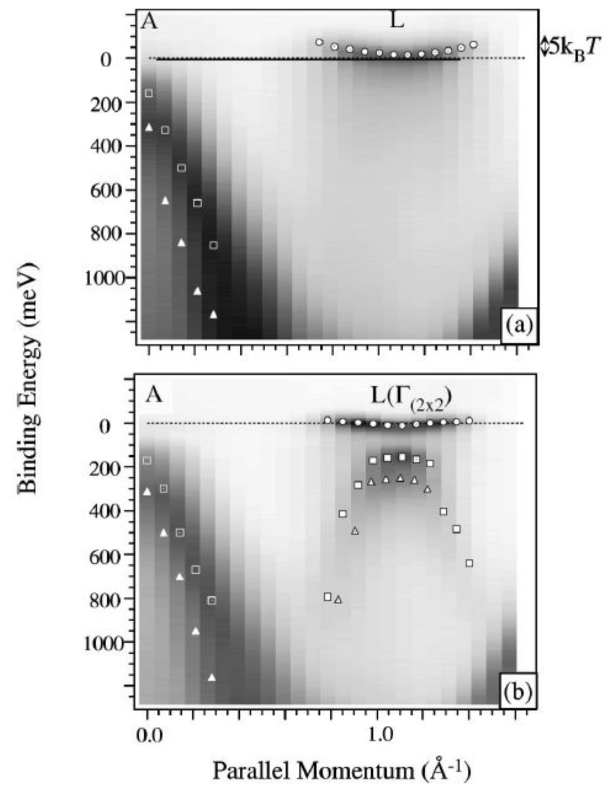


347
298
1132
300 K
225 K
200 K
150 K
80 K
50 K
10 K
0.10
0.08
0.06
0.04
0.02
0.00
100
1000
10000
Im[-1/ε(ω)]
ω (cm^{-1})



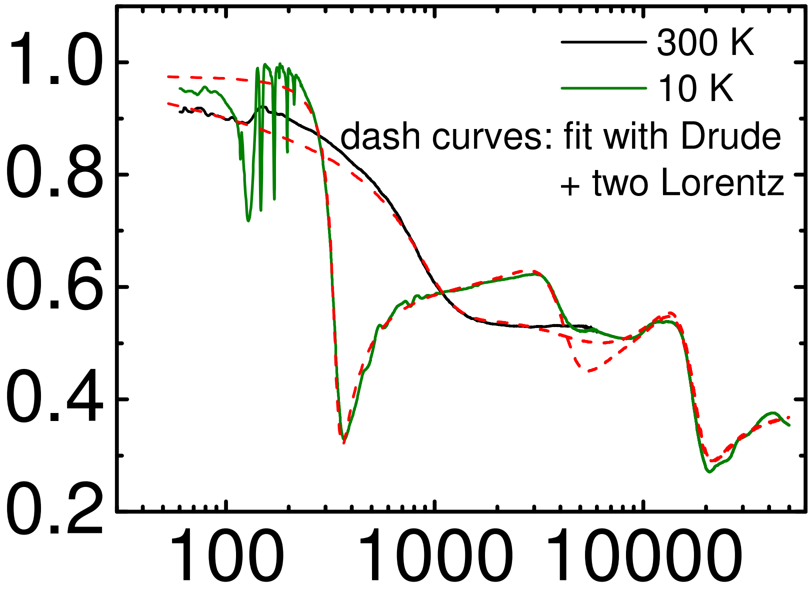
Drude

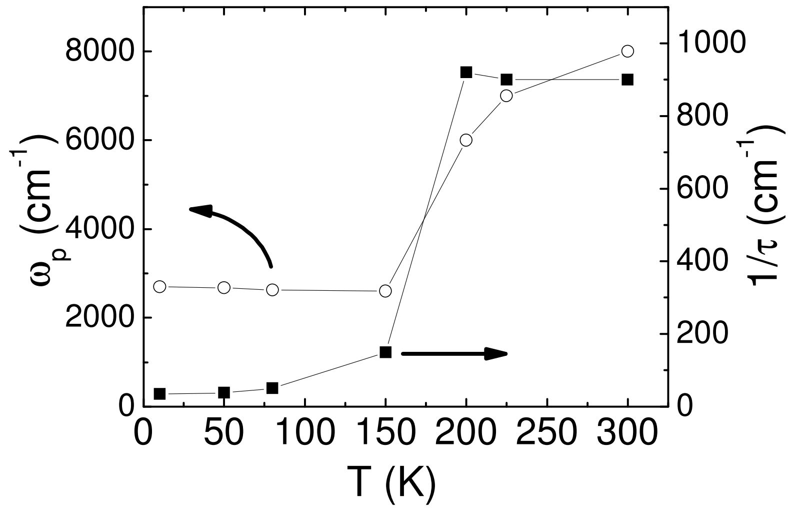
CDW gap



Free carriers with very long relaxation time exist in the CDW gapped state

⇨ FS is not fully gapped??





$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{i=1}^{2} \frac{S_i^2}{\omega_i^2 - \omega^2 - i\omega/\tau_i}. \quad (1)$$

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

- 1T-TiSe2 is a semimetal with very low carrier density at all T
- Carrier density changes with T, decreases from room T to 150 K then increases slightly with further decreasing T
- Development of an energy gap ~0.15 eV below 200 K
- Dramatic different carrier damping at different T

Excitonic Phases W. Kohn, PRL 67

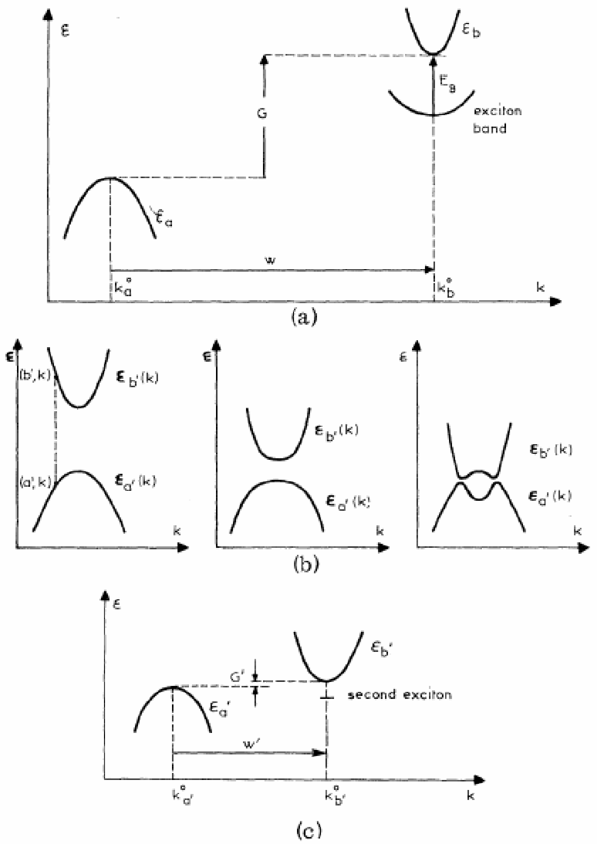


FIG. 1. The insulating side. (a) Energy bands and exciton band of the normal insulator. (b) The new energy bands after the first excitonic transition for successive values of the external parameter (e.g., pressure). (c) The second excitonic instability.

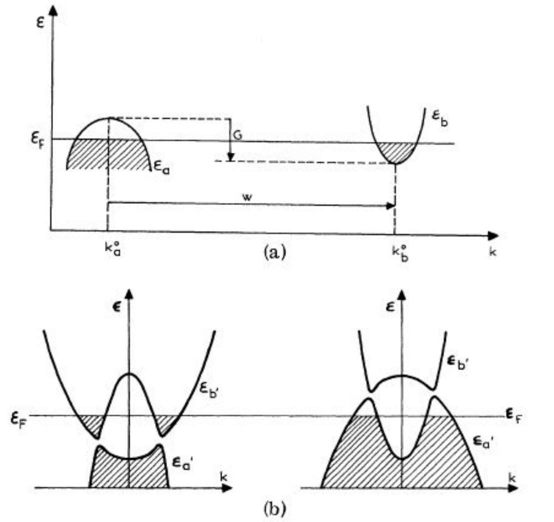


FIG. 2. The metallic side. (a) Energy bands of the normal semimetal. (b) Energy bands after the first Overhauser transition for two different directions of k.

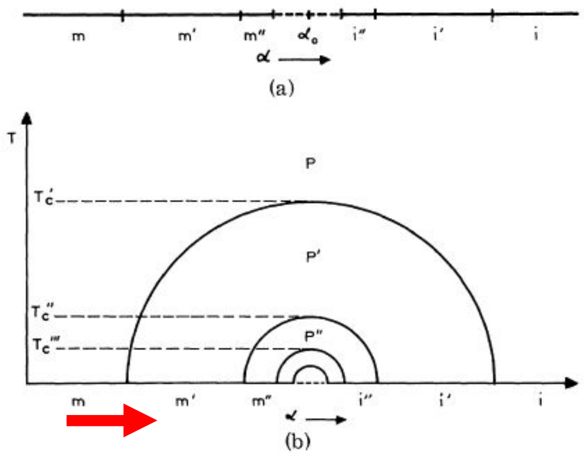
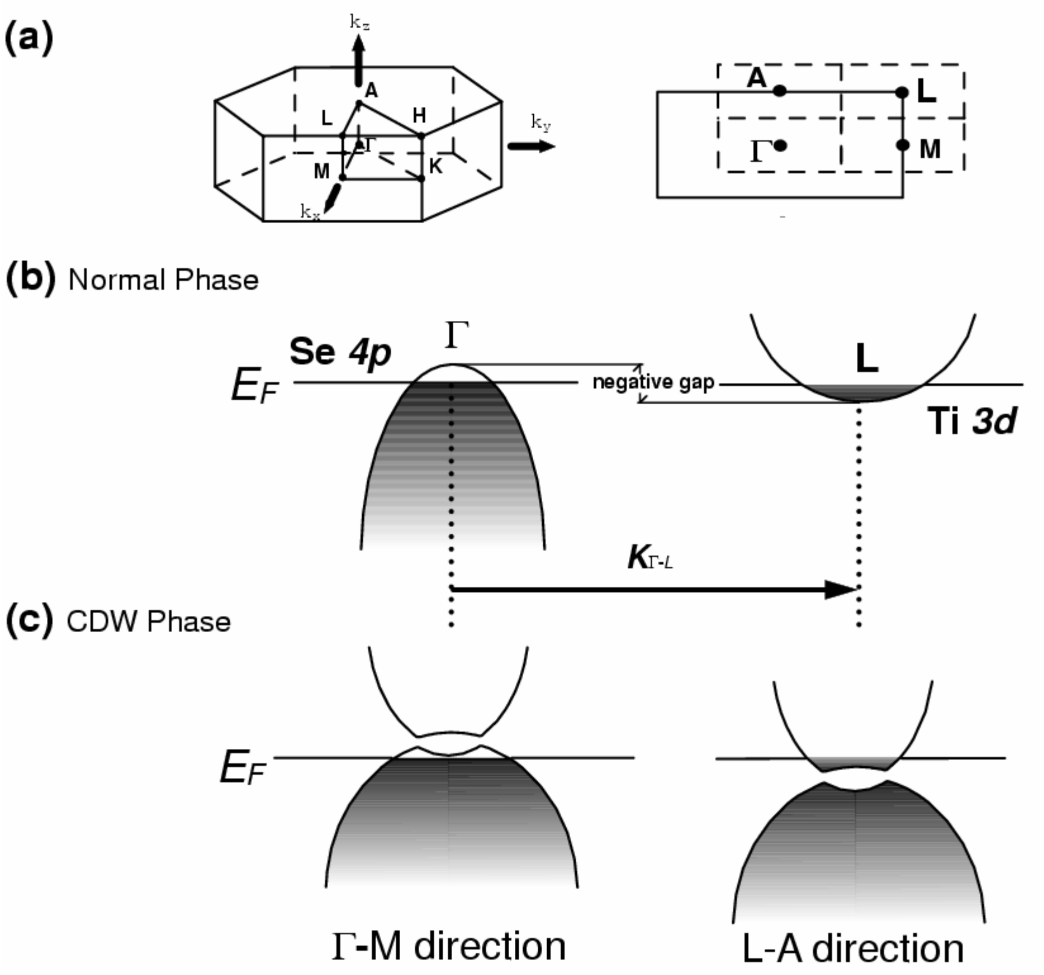
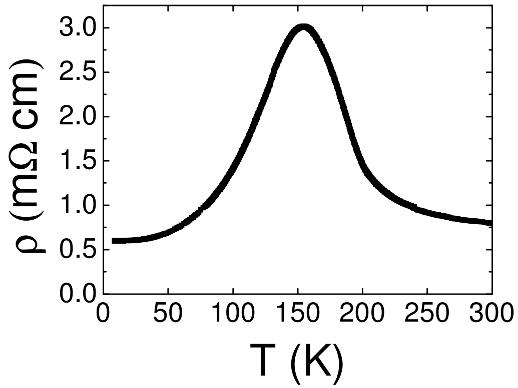


FIG. 3. The excitonic phases. (a) Succession of phases, at $T=0°$, for different values of α; m, metallic; i, insulating. The dotted interval contains an infinity of m and i phases. (b) Total phase diagram, showing an infinity of nested phases.

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



Exciton-driven CDW



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

$$R_H = \frac{1}{e}\frac{n_h\mu_h^2 - n_e\mu_e^2}{(n_h\mu_h + n_e\mu_e)^2},$$

$$\sigma = e(n_h\mu_h + n_e\mu_e)$$

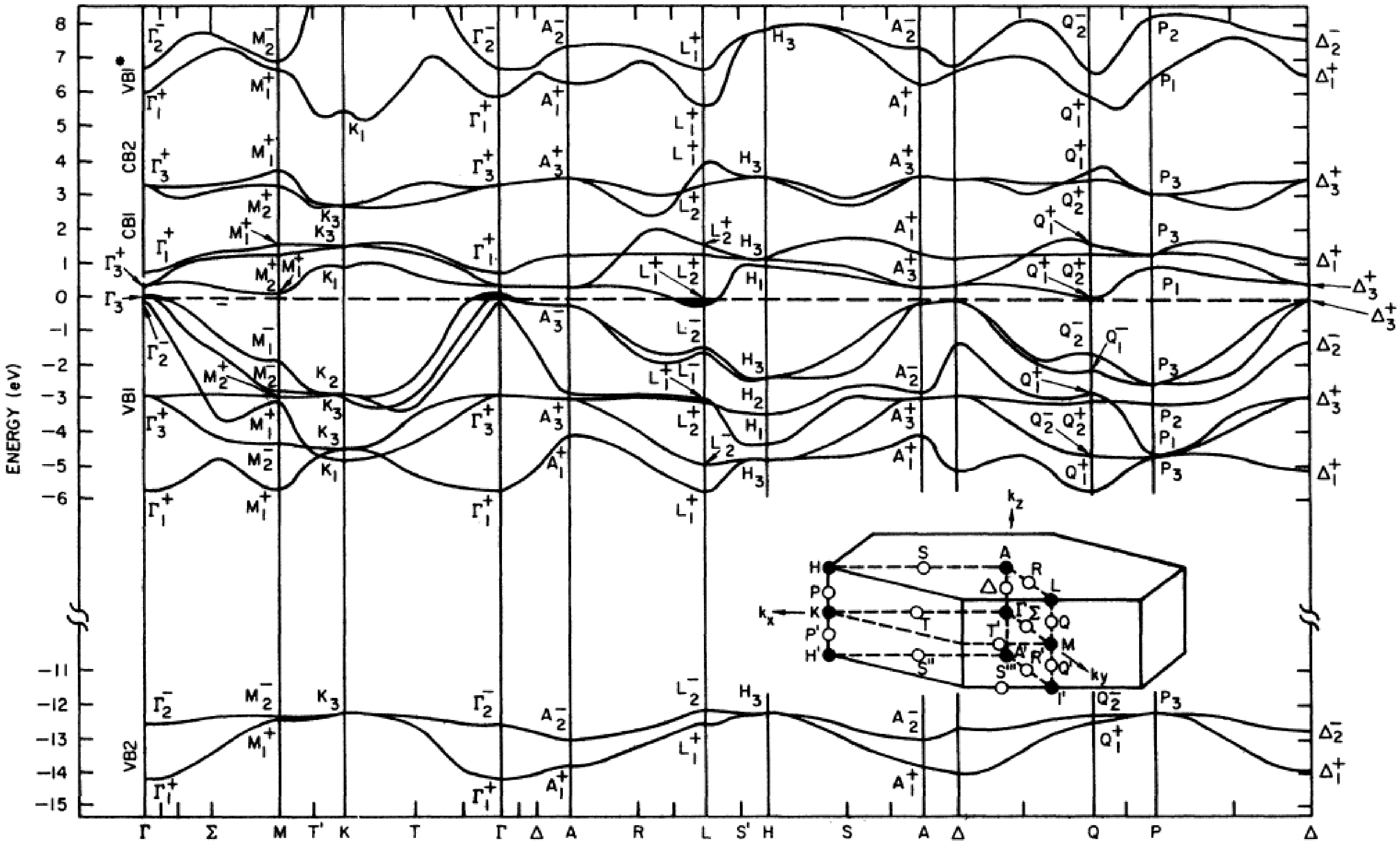
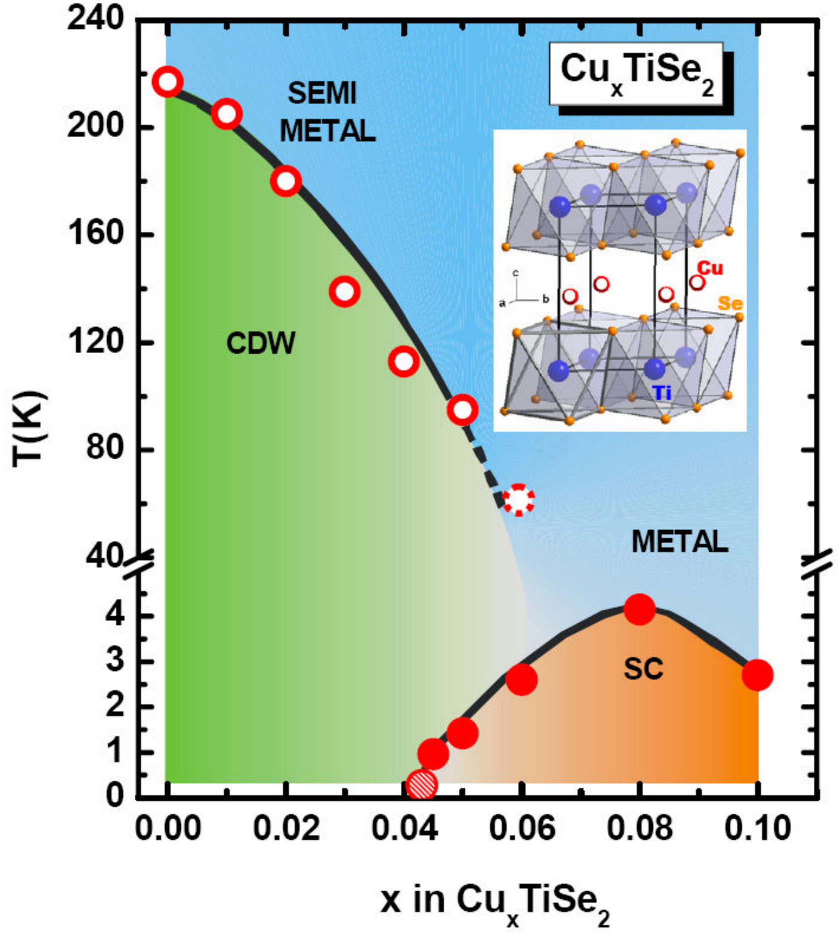
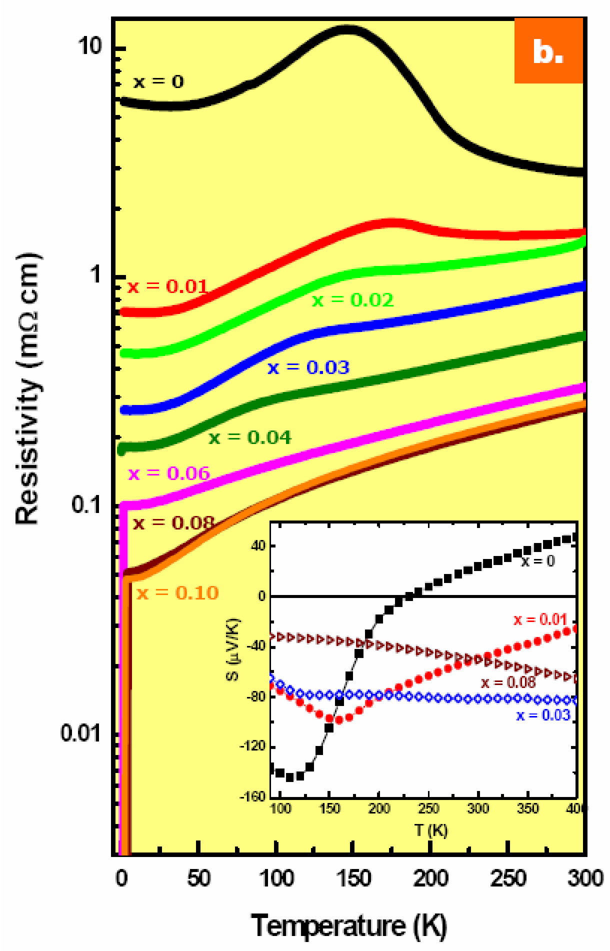
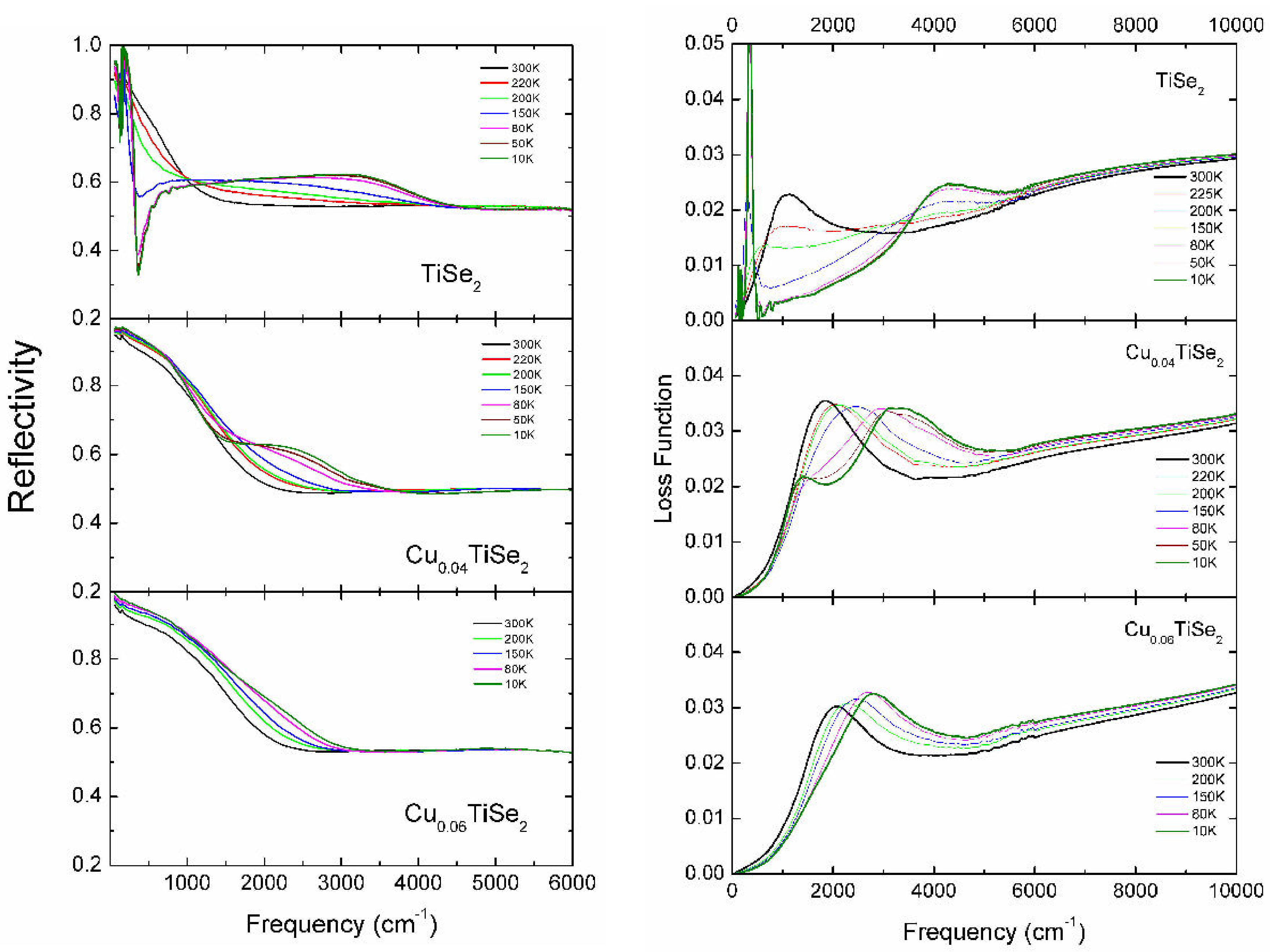


FIG. 1. Energy-band structure of $TiSe_2$ in the local exchange and correlation model.

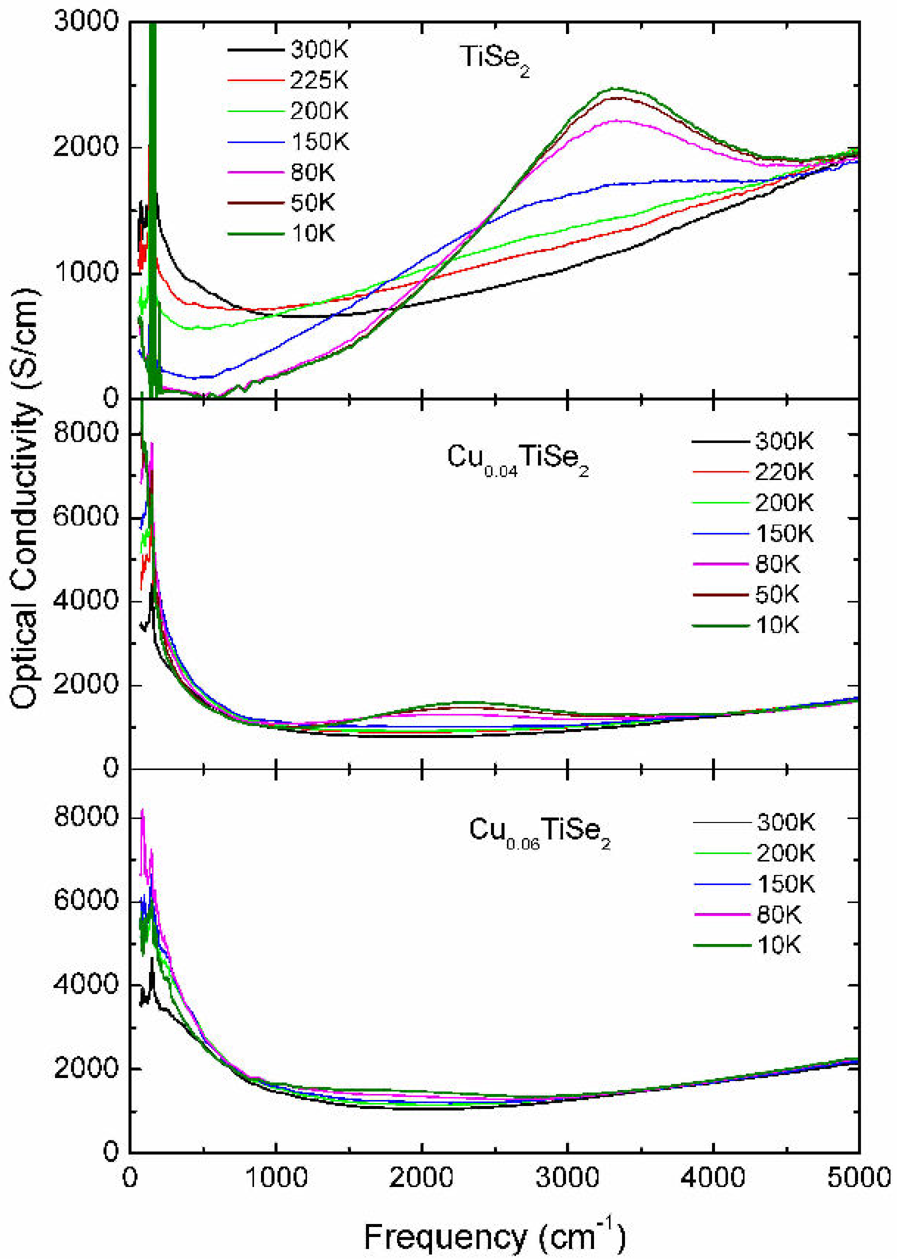
Cu-doped CuxTiSe2





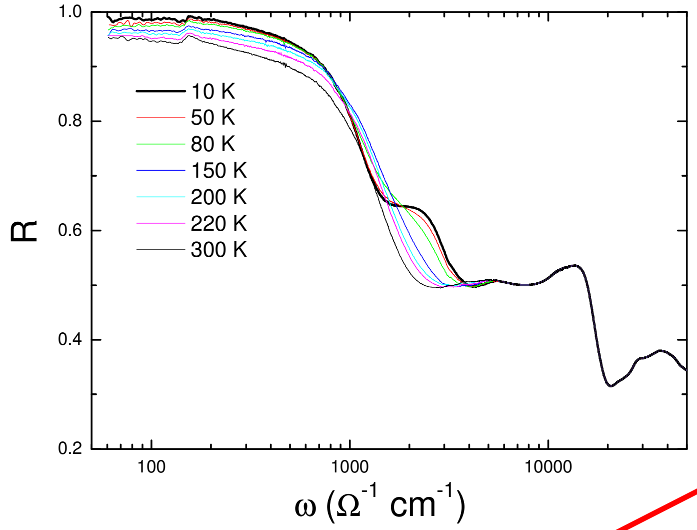


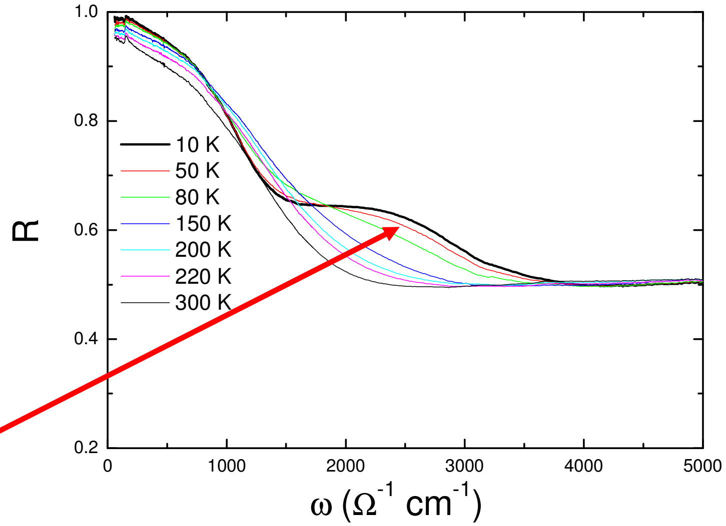
Reflectivity
Frequency (cm-1)
TiSe2
Cu0.04TiSe2
Cu0.06TiSe2
300K
220K
200K
150K
80K
50K
10K
Loss Function
225K



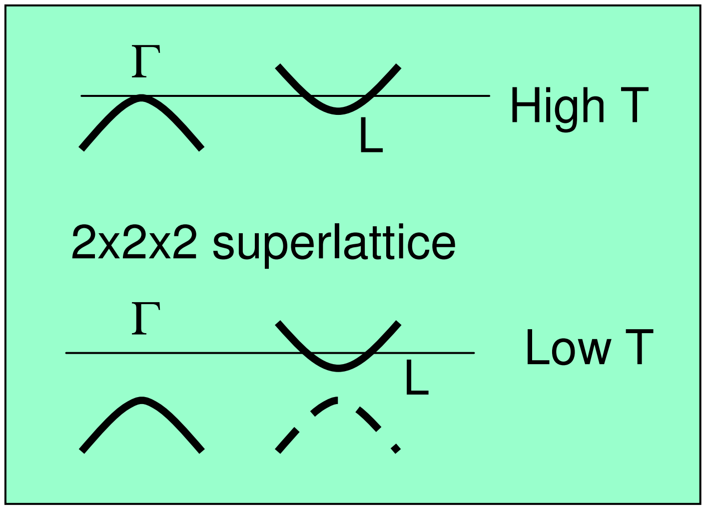
TiSe$_2$
300K
225K
200K
150K
80K
50K
10K
Cu$_{0.04}$TiSe$_2$
300K
220K
200K
150K
80K
50K
10K
Cu$_{0.06}$TiSe$_2$
300K
200K
150K
80K
10K
Optical Conductivity (S/cm)
Frequency (cm^{-1})

$Cu_{0.04}TiSe_2$ crystal, Tc~3 K

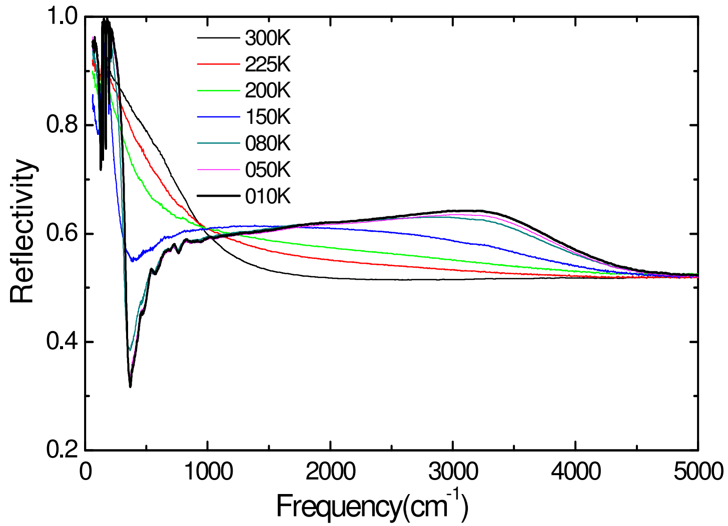




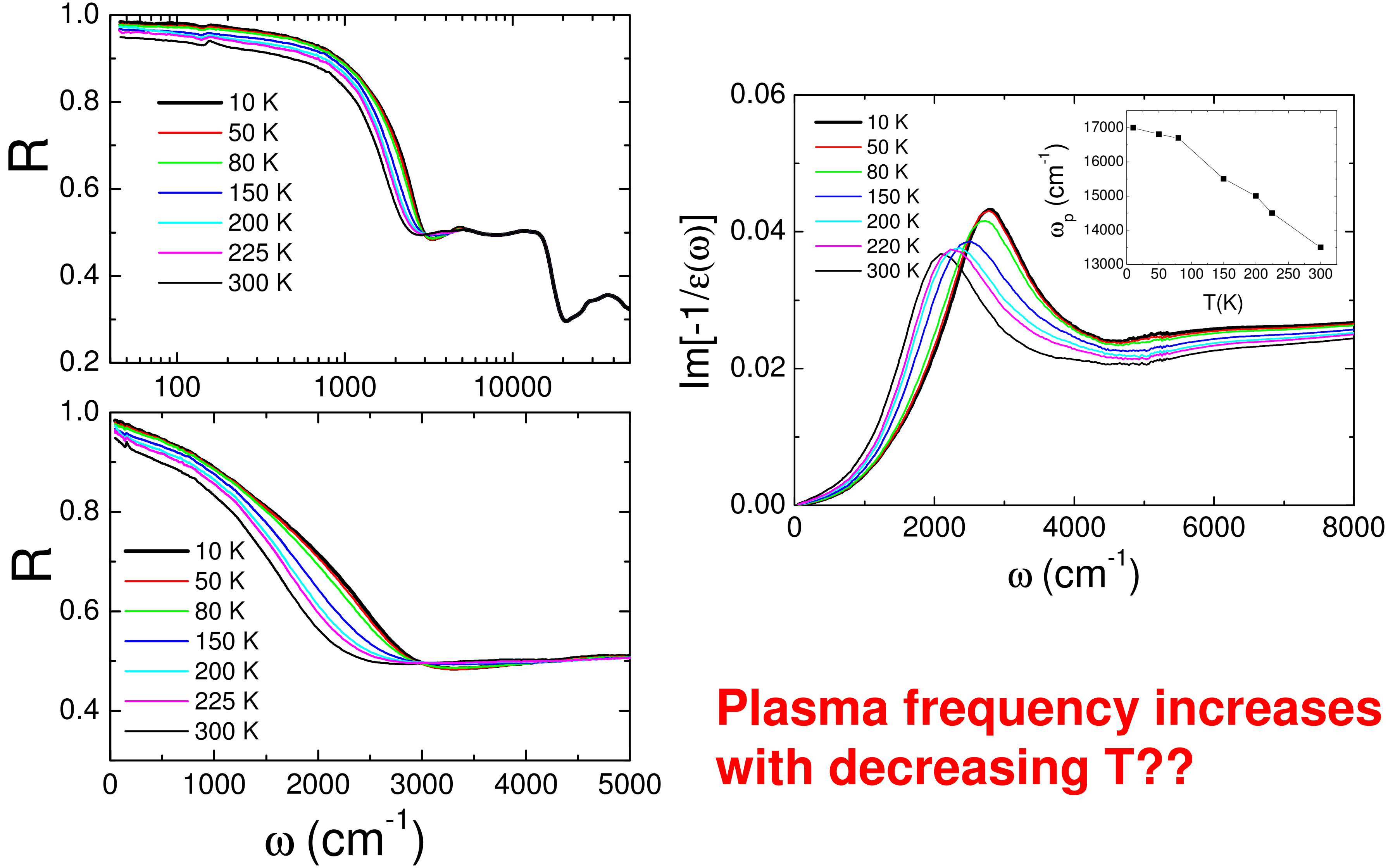
CDW gap still exists



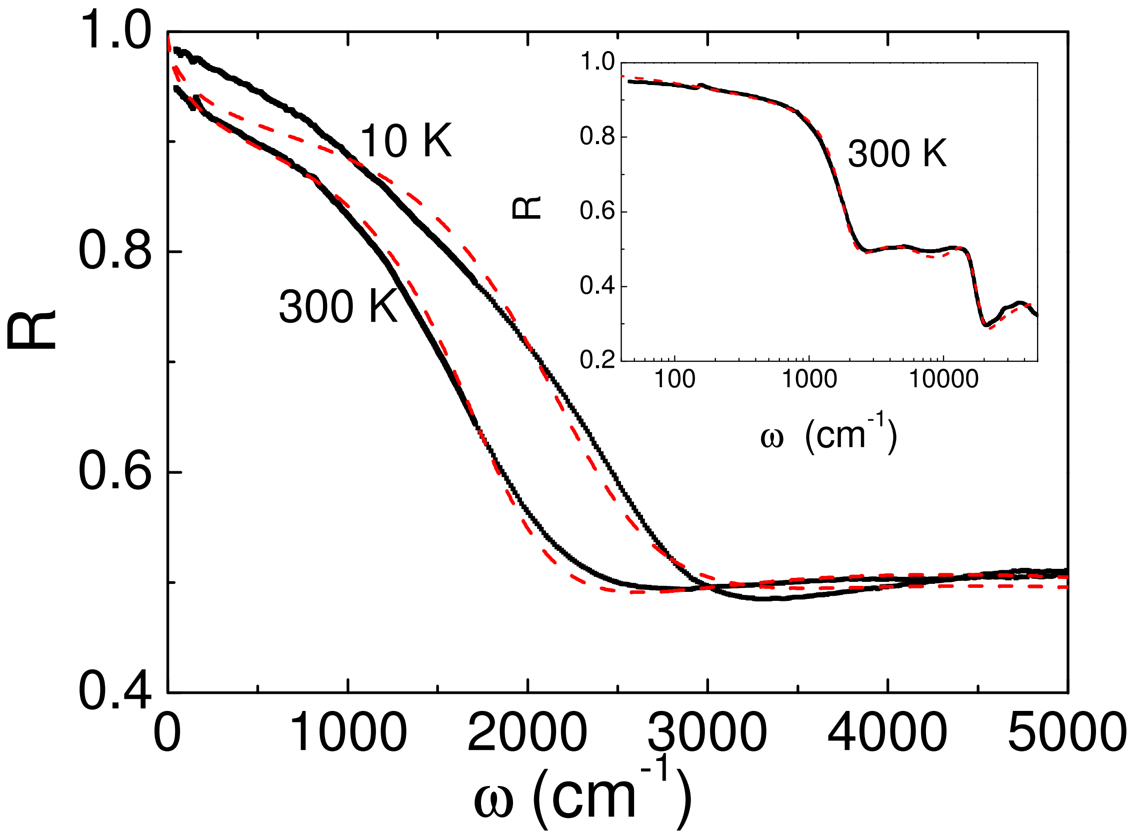
Compared with CuTi2



X=0.07

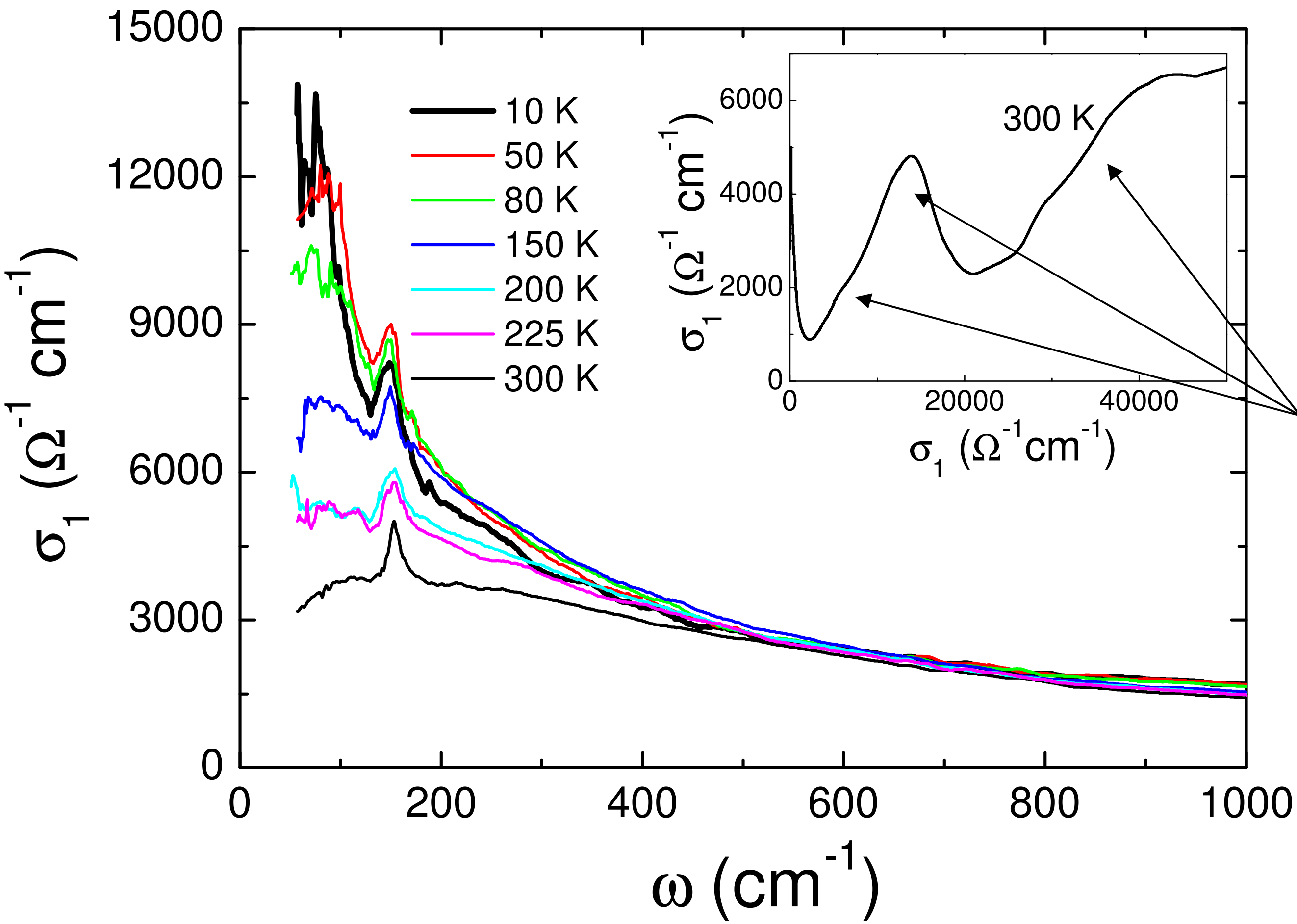


Plasma frequency increases with decreasing T??



$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{i=1}^{2} \frac{S_i^2}{\omega_i^2 - \omega^2 - i\omega/\tau_i}. \qquad (1)$$

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



Interband transitions from Se 4p band to unoccupied part of Ti 3d band

Plasma frequency increases with decreasing T??

$$\omega_p^2 = \frac{4\pi n e^2}{m^*}$$

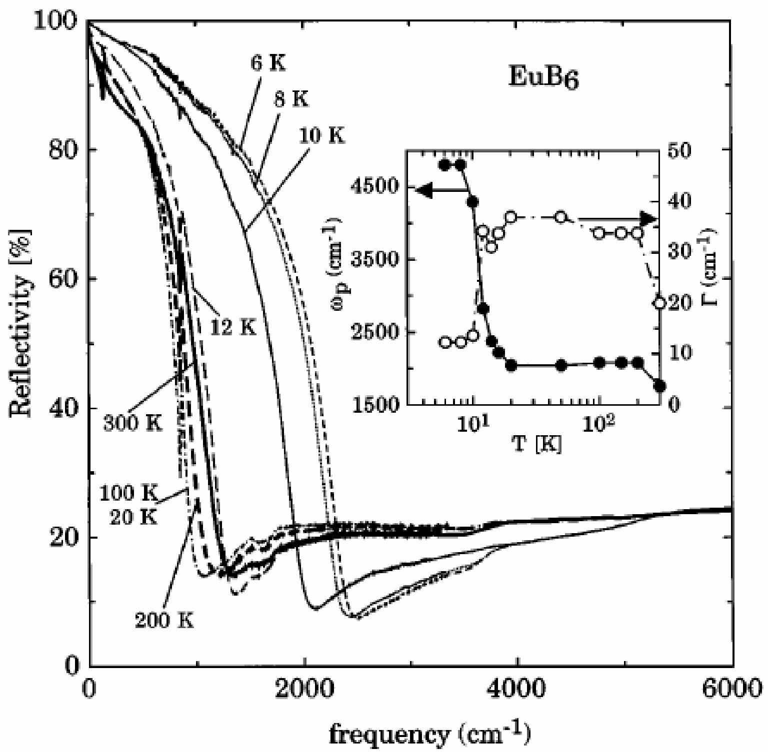
In terms of two bands:

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

- n increases with decreasing T??
- m* decreases with decreasing T, undressing effect??

Low-Temperature Anomalies and Ferromagnetism of EuB_6

L. Degiorgi,[1] E. Felder,[1] H. R. Ott,[1] J. L. Sarrao,[2] and Z. Fisk[2]
[1]*Laboratorium für Festkörperphysik, ETH Hönggerberg, 8093 Zürich, Switzerland*
[2]*National High Magnetic Field Laboratory, Florida State University, 1800 Paul Dirac Drive, Tallahassee, Florida 32306*
(Received 21 April 1997)

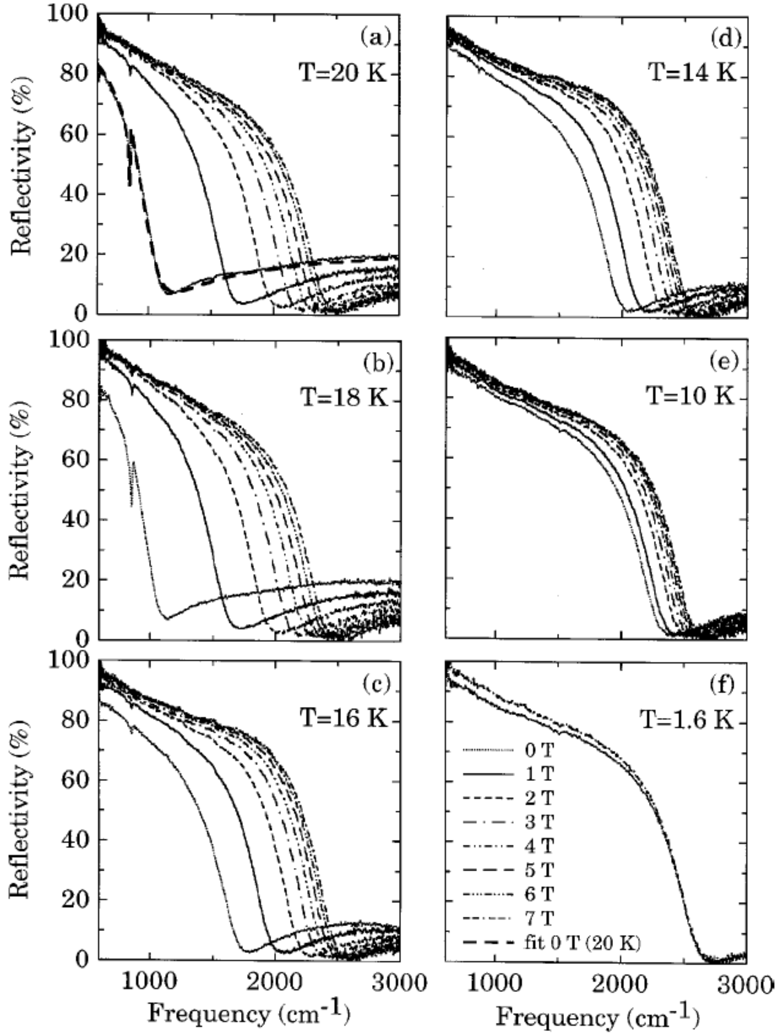


PHYSICAL REVIEW B, VOLUME 65, 121102(R)

Scaling between magnetization and Drude weight in EuB_6

S. Broderick, B. Ruzicka,* L. Degiorgi, and H. R. Ott
Laboratorium für Festkörperphysik ETH Zurich, CH-8093 Zurich, Switzerland

J. L. Sarrao[†] and Z. Fisk
NHMFL-FSU, Tallahassee, Florida 32306



Ferromagnetism from Undressing

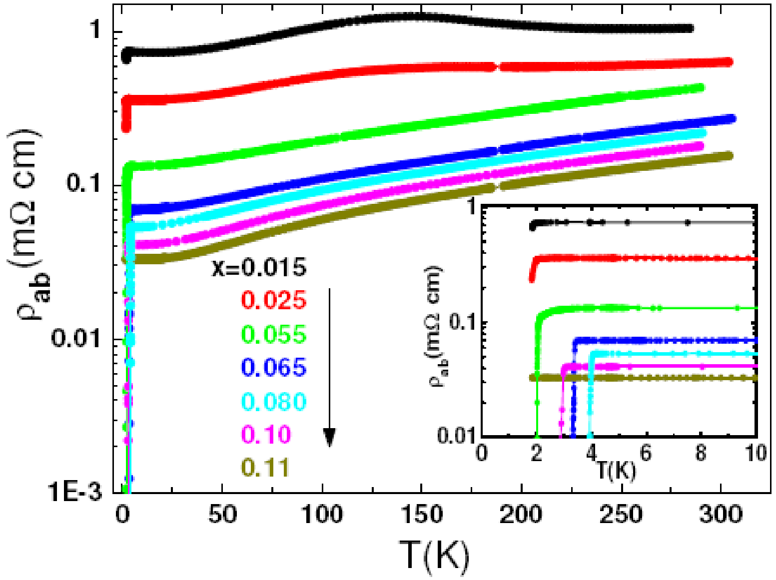
J. E. Hirsch
Department of Physics, University of California, San Diego
La Jolla, CA 92093-0319
(November 19, 2002)

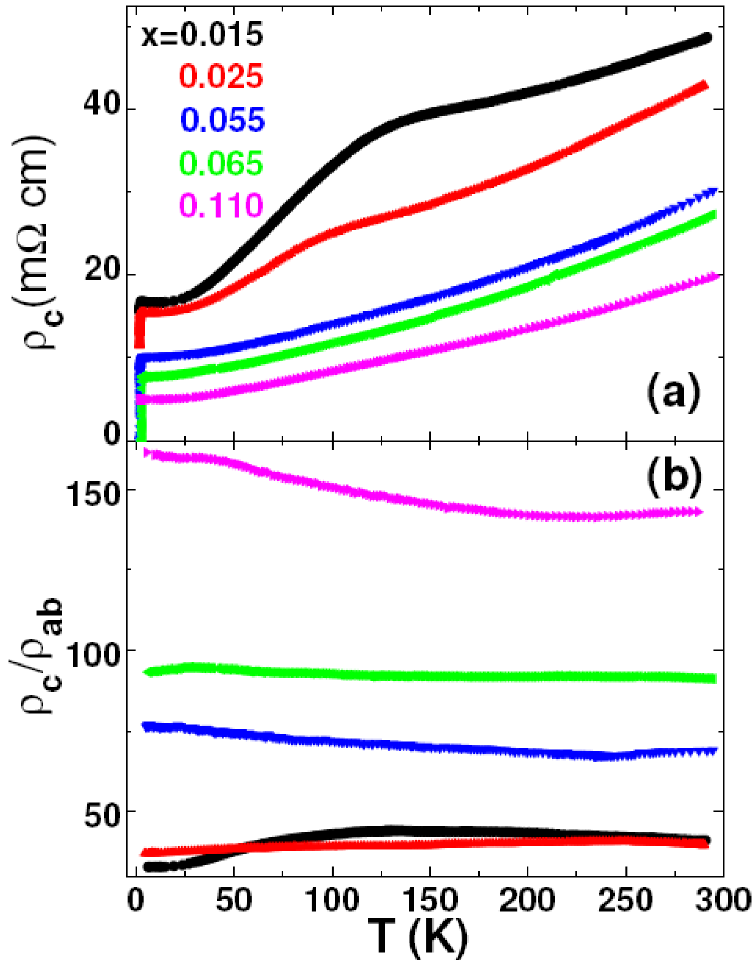
We have recently proposed that superconductivity may be understood as driven by the undressing of quasiparticles as the superconducting state develops. Similarly we propose here that ferromagnetism in metals may be understood as driven by the undressing of quasiparticles as the ferromagnetic state develops. In ferromagnets, the undressing is proposed to occur due to the reduction in *bond charge* caused by spin polarization, in contrast to superconductors where the undressing is proposed to occur due to the reduction in *site charge* caused by (hole) pairing. The undressing process manifests itself in the one and two-particle Green's functions as a transfer of spectral weight from high to low frequencies. Hence it should have universal observable consequences in one- and two-particle spectroscopies such as photoemission and optical absorption.

Cond-mat/0007454 (PRB (2000))

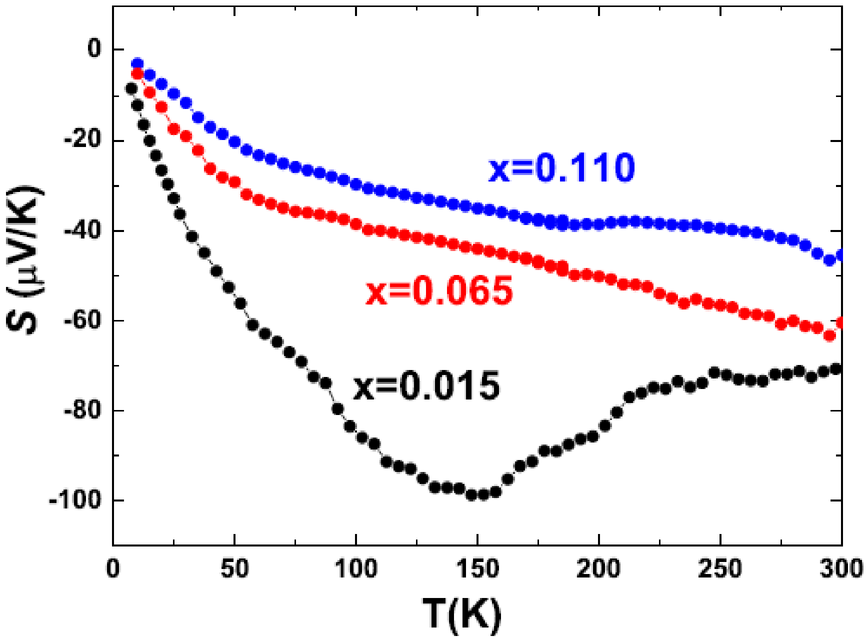
Transport properties in Cu_xTiSe_2 ($0.015 \leq x \leq 0.110$) Single Crystal

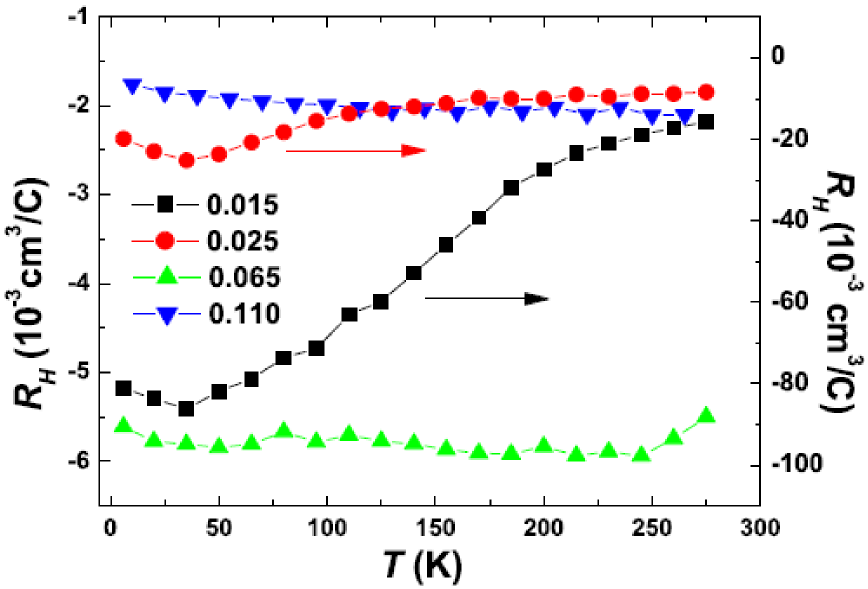
G. Wu, H. X. Yang, L. Zhao, X. G. Luo, T. Wu, G. Y. Wang and X. H. Chen*
Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China





Cond-mat/0703645





Hall coefficient is almost T-independent for superconducting sample!!