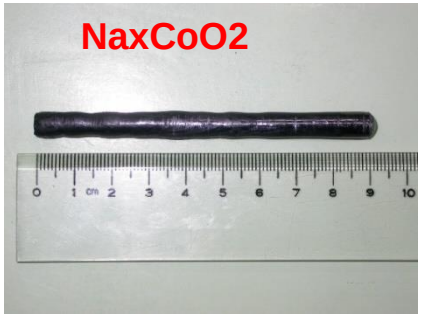
# Optical spectroscopy studies of Na2Ti2Pn2O (Pn=Sb, As) and Ba2Ti2Fe2As4O

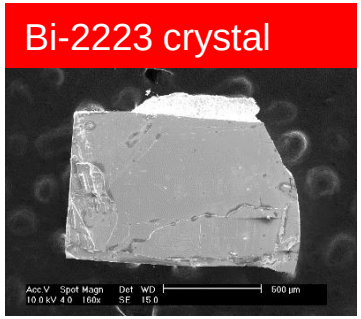
**Nan-Lin Wang**

International Center for Quantum Materials (ICQM)
Peking University

Work done with Y. Huang, Y. G. Shi, H. P. Wang, T. Dong, G. H. Cao

# Single crystal growth and characterizations



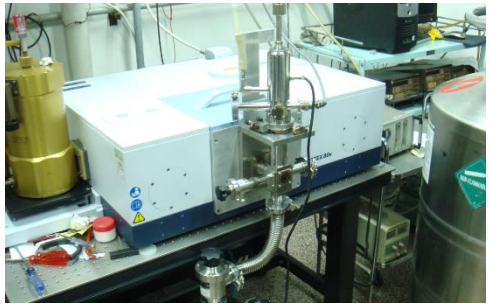





Floating zone, arc-melting furnaces, numerous tube and box furnaces

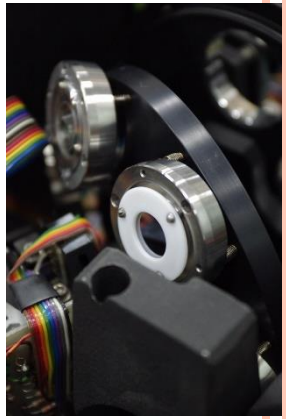
# Spectrometers and frequency range in our lab

- Bruker 80v: 30 - 40000 cm-1
- Bruker 66v/s: 30 - 30000 cm-1



- Bruker 113v: 15 – 8000 cm-1 (thick si-beam splitter with Si-bolometer)

Si-BMS



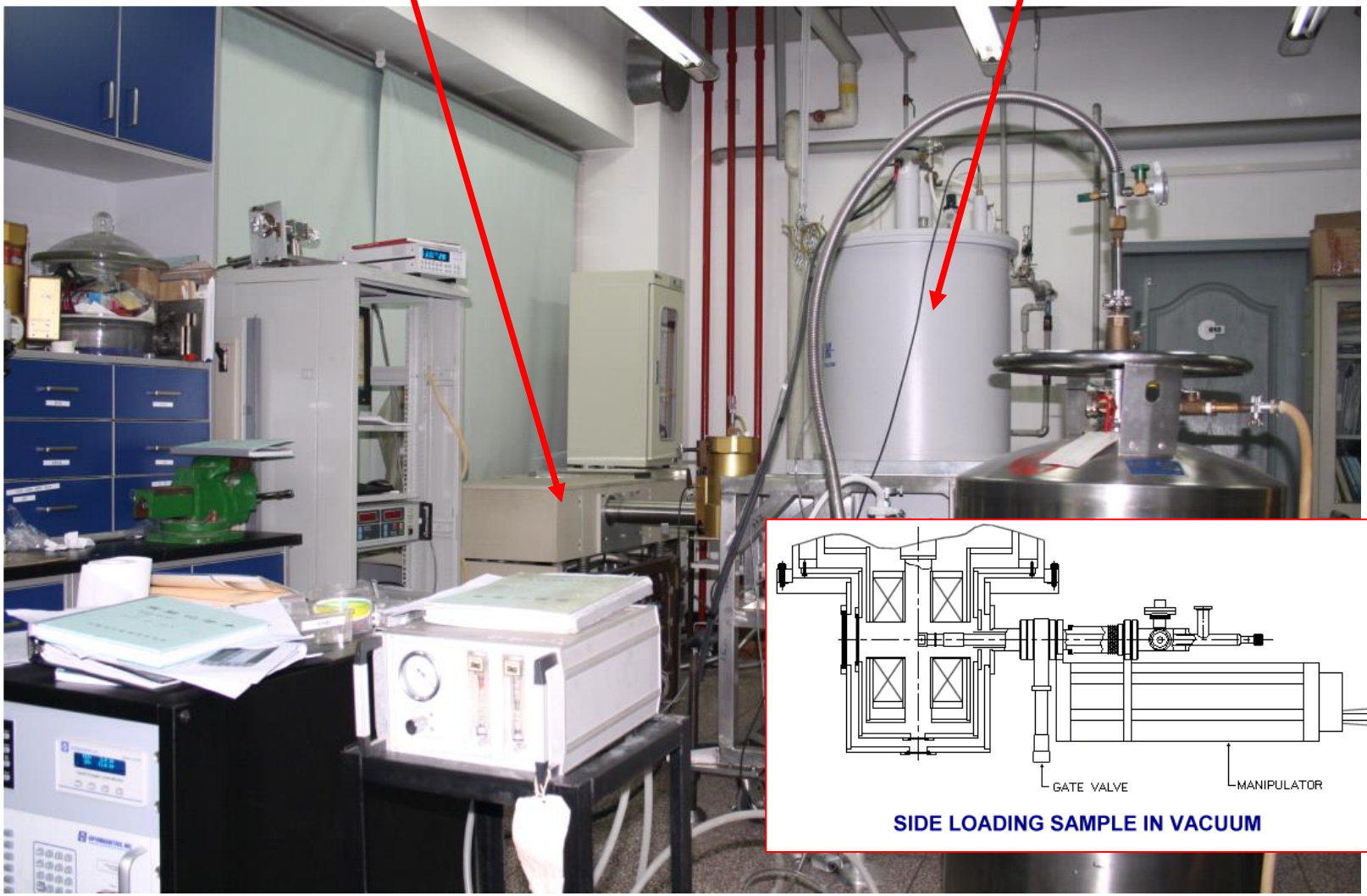
- Grating type spectrometer: 6000-50000 cm-1

In-situ gold- or aluminum-deposit technique

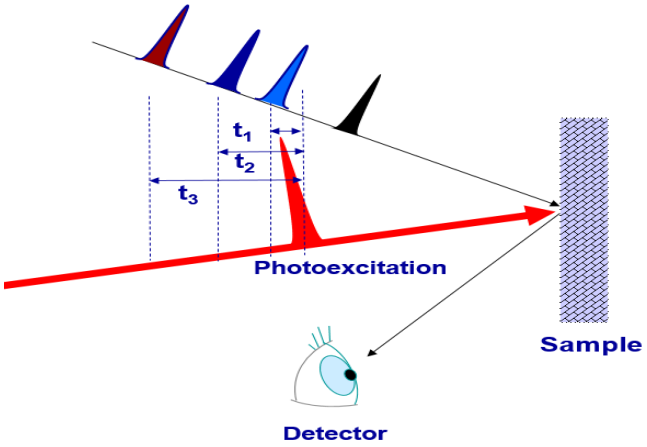
# Optical measurement under magnetic field

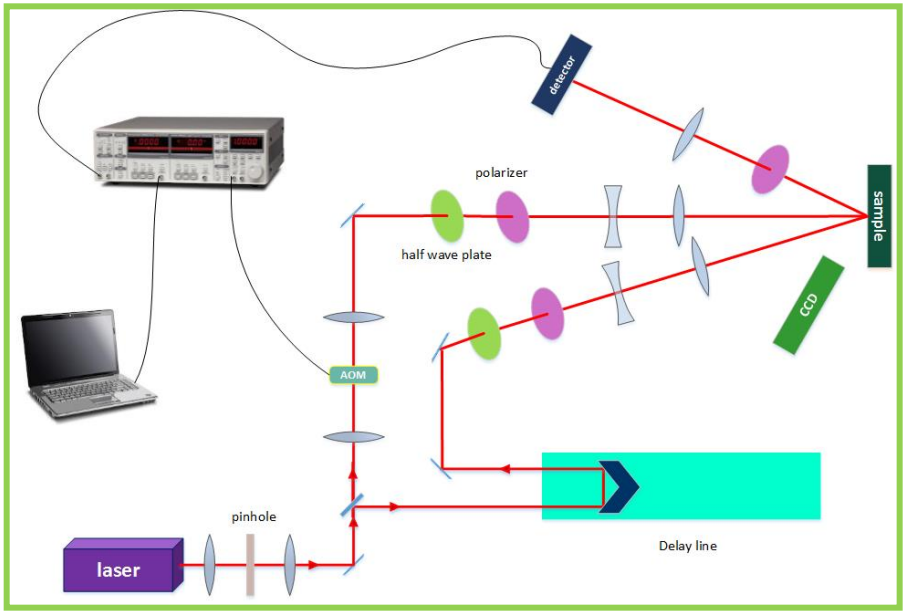
Bruker 113v spectrometer

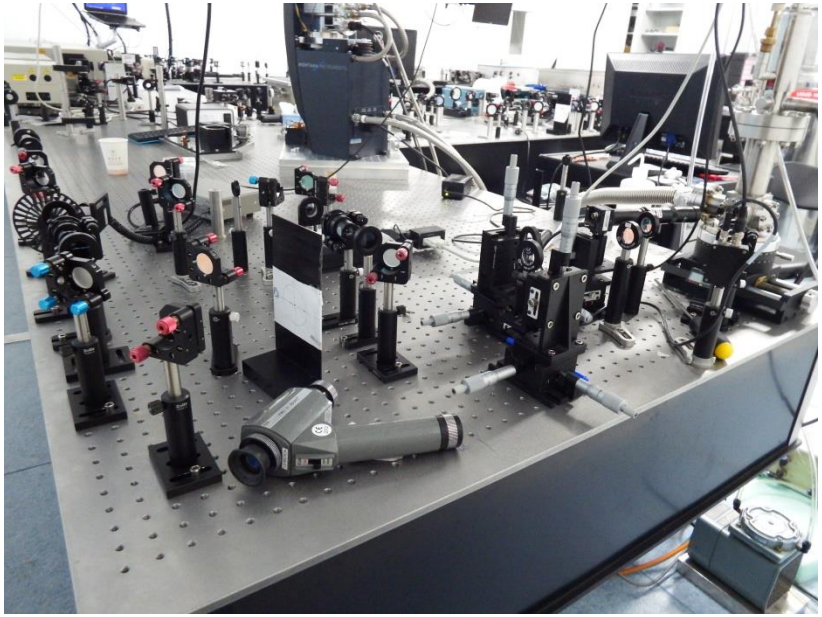
(10 Tesla split coils from Cryomagnetic Inc.)



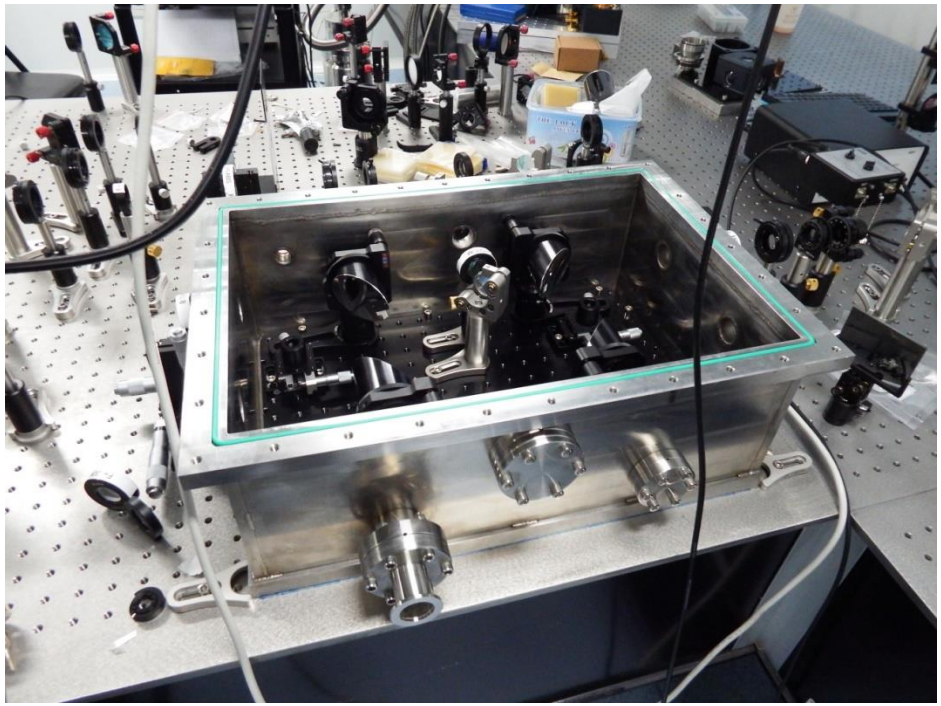
# Pump-probe experiment based on femtosecond laser

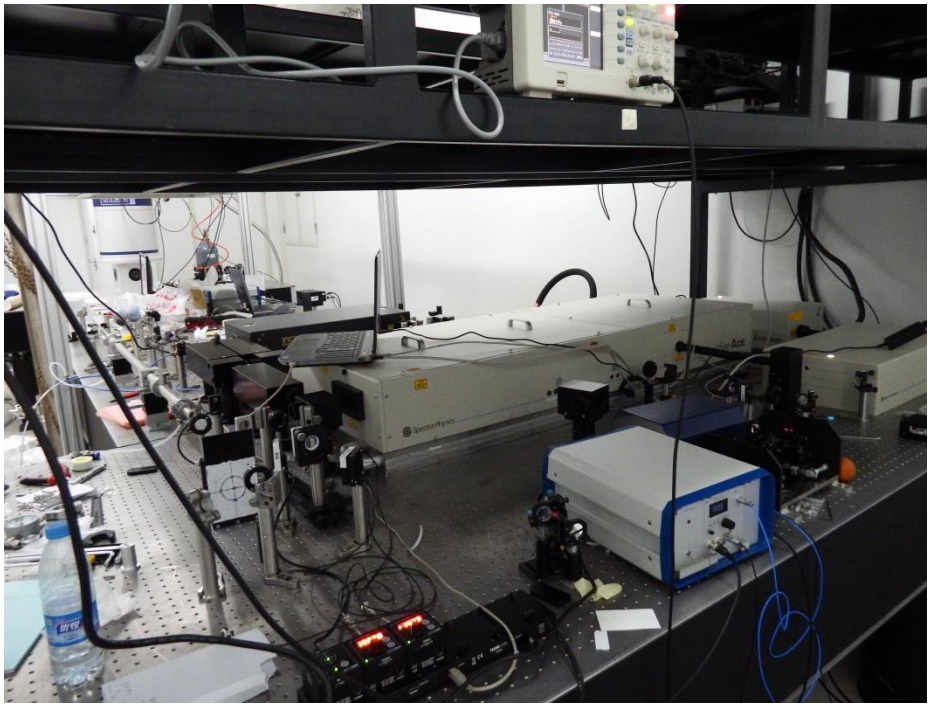


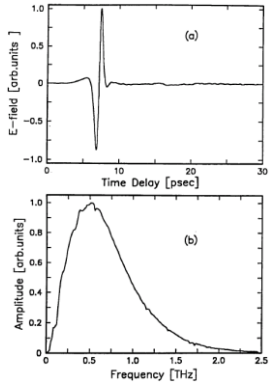
# THz time domain spectroscopy





We are working and developing projects:

- Optical (IR) pump-THz probe
- Mid-IR pump- THz probe
- ……

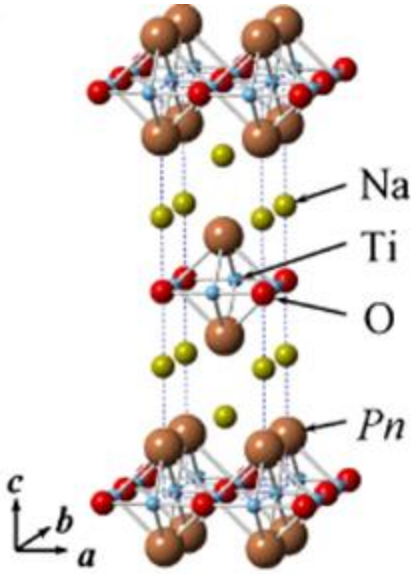


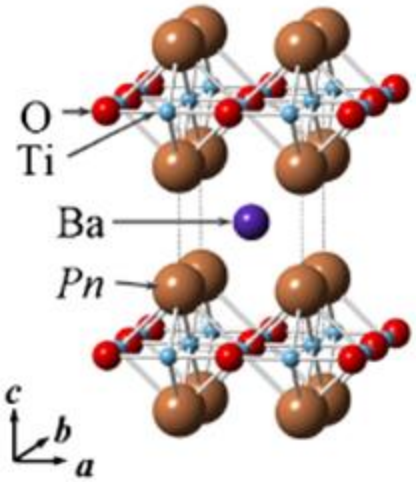
# Outline:

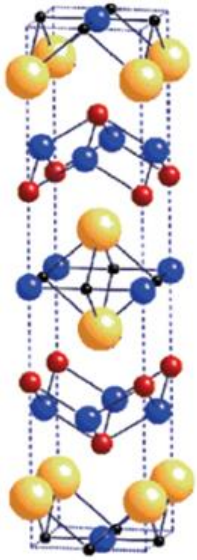
- Introduction about materials
- Optical spectroscopy study on density wave (DW) order in Na2Ti2Sb2O
- Two DW orders in Na2Ti2As2O？
- Coexistence of DW and superconductivity in Ba2Ti2Fe2As4O

Y. Huang et al.,Phys. Rev. B 87, 100507 (R) (2013);
Y. G. Shi et al. PRB 88, 144513 (2013);
Y. Huang et al. PRB 89, 155120 (2014);
H. P. Wang et al. PRB 90, 144508 (2014)

# $Ti_2Pn_2O$-type structure



Big structure family

- The spacer layer could be: Na2, Ba, La2O2, Sr2F2, ……
- Ti could be other 3d transition metal elements, e.g. Fe, Co,…

# $Fe_2Se_2O$， $Co_2Se_2O$ …, ----**Orbital selective Mottness**

PRL **104,** 216405 (2010) PHYSICAL REVIEW LETTERS week ending 28 MAY 2010

## Band Narrowing and Mott Localization in Iron Oxychalcogenides $La_2O_2Fe_2O(Se, S)_2$

Jian-Xin Zhu,[1] Rong Yu,[2] Hangdong Wang,[3] Liang L. Zhao,[2] M. D. Jones,[4] Jianhui Dai,[3] Elihu Abrahams,[5,*] E. Morosan,[2] Minghu Fang,[3] and Qimiao Si[2]

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[2]*Department of Physics & Astronomy, Rice University, Houston, Texas 77005, USA*
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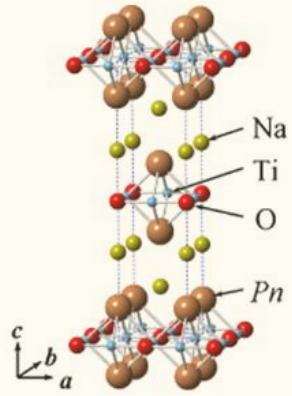
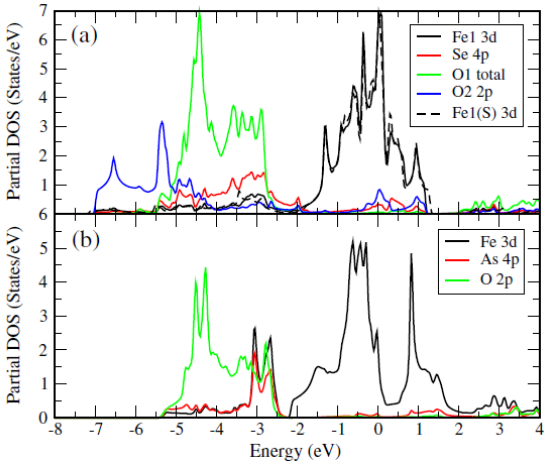
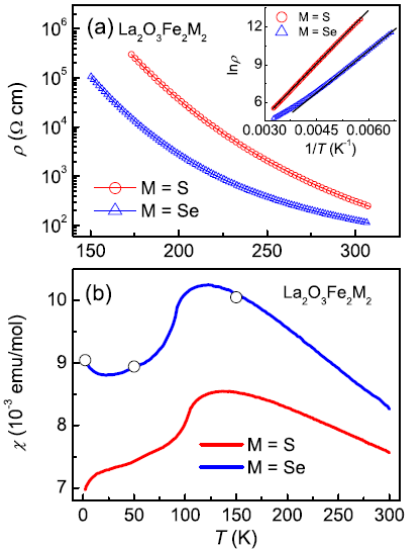
(Received 24 December 2009; published 28 May 2010)




(Ti,As) ⟹ (Fe,Se)

$Na_2$ layer ⟹ $La_2O_2$

PHYSICAL REVIEW B **84**, 205212 (2011)

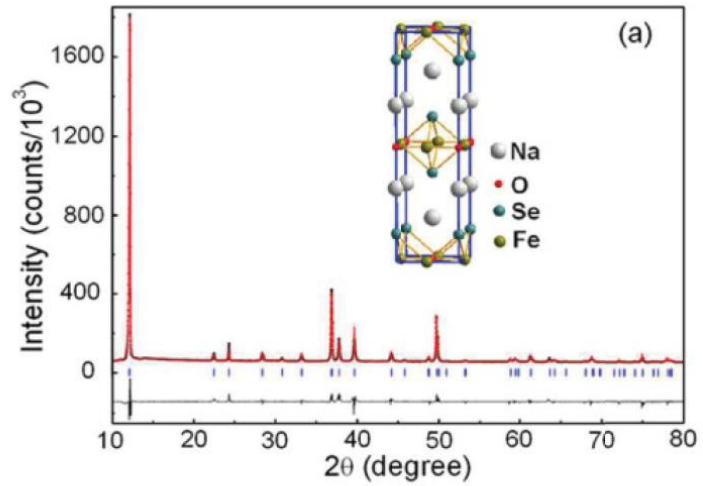
# Synthesis, structure, and magnetic properties of the layered iron oxychalcogenide $Na_2Fe_2Se_2O$

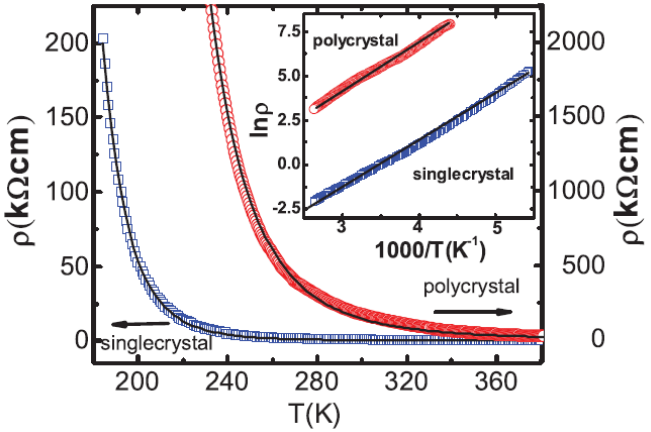
J. B. He,[1] D. M. Wang,[1] H. L. Shi,[2] H. X. Yang,[2] J. Q. Li,[2] and G. F. Chen[1,2,*]

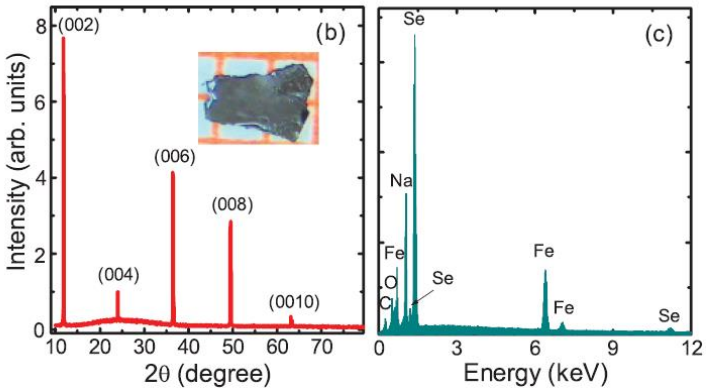
[1]*Department of Physics, Renmin University of China, Beijing 100872, People's Republic of China*

[2]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

(Received 26 April 2011; revised manuscript received 9 October 2011; published 15 November 2011)

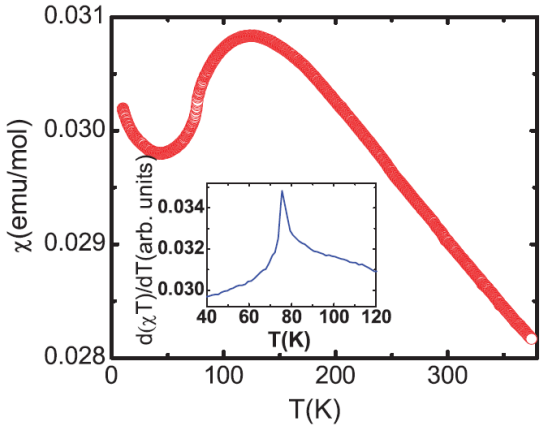


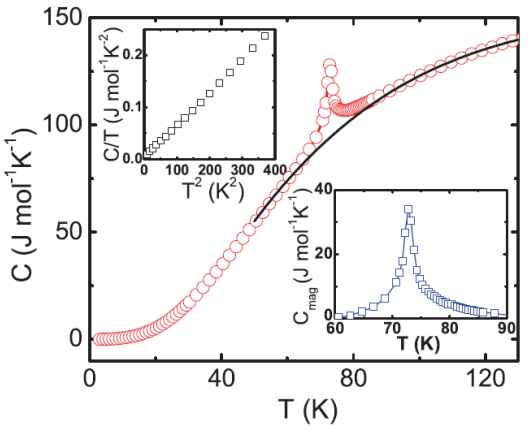







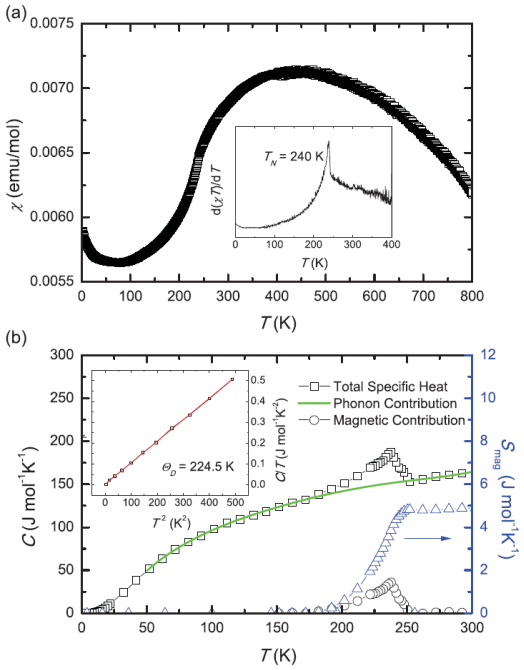


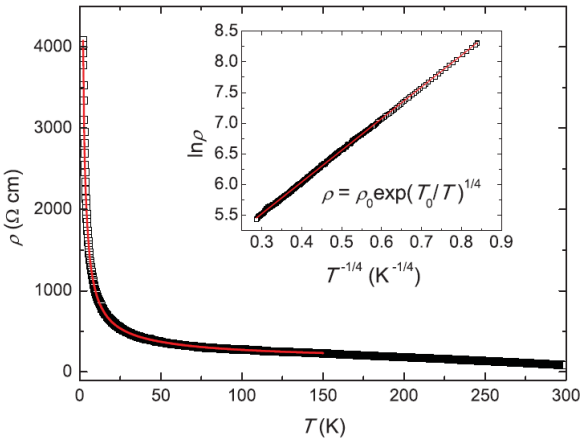



PHYSICAL REVIEW B **86**, 014411 (2012)

# $BaFe_2Se_2O$ as an iron-based Mott insulator with antiferromagnetic order

Fei Han,[1,2] Xiangang Wan,[1] Bing Shen,[1,2] and Hai-Hu Wen[1,*]



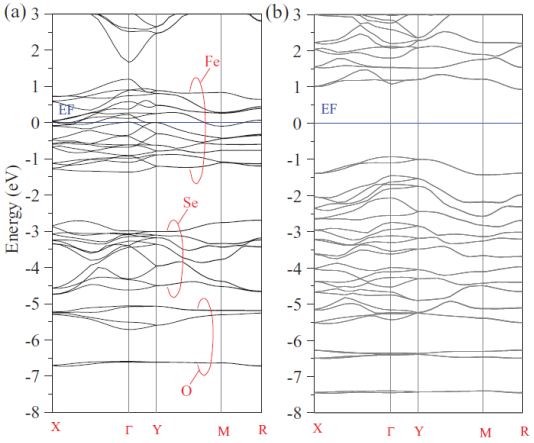



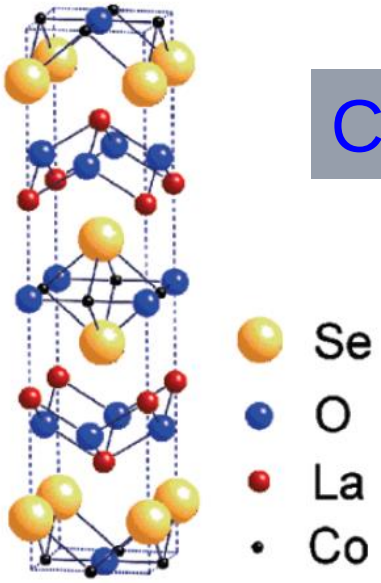

FIG. 4. (Color online) Band structure from LDA calculation, and LDA + $U$ calculation with $U = 6.0$ eV.

PHYSICAL REVIEW B **86**, 195133 (2012)

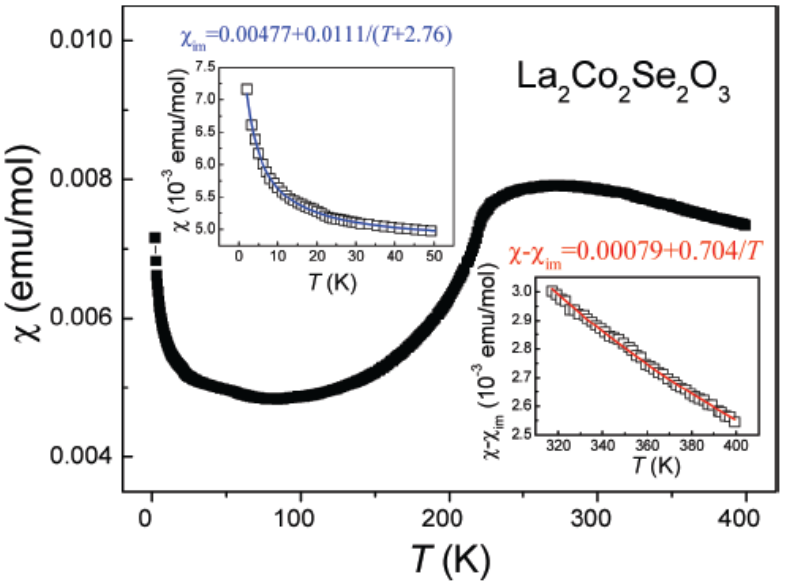
# Structure and physical properties of the layered iron oxychalcogenide $BaFe_2Se_2O$

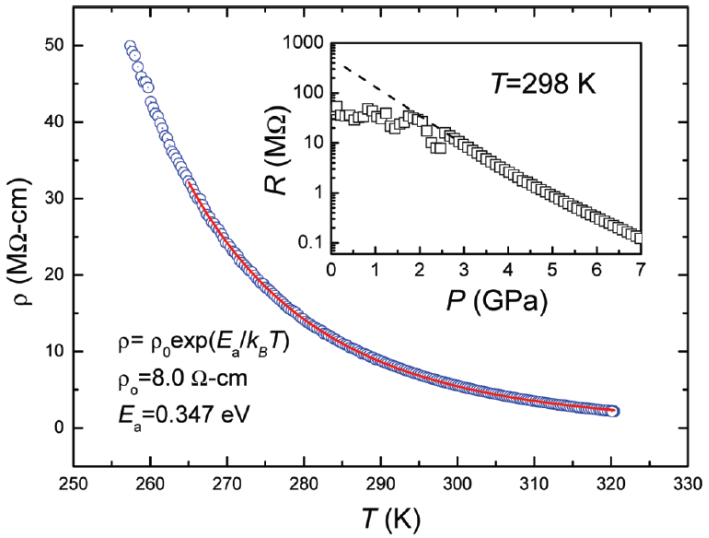
Hechang Lei(雷和畅),[1] Hyejin Ryu(류혜진),[1,2] V. Ivanovski,[3] J. B. Warren,[4] A. I. Frenkel,[5] B. Cekic,[3] Wei-Guo Yin(尹卫国),[1] and C. Petrovic[1,2]

# $LA_2CO_2SE_2O_3$: 反铁磁基态, $T_N$=220K




$Co_2Se_2O$ layer




**Unfortunately, very difficult to dope charge carriers!**

J. Am. Chem. Soc. 132, 7069 (2010).

# Na2Ti2Pn2O (Pn=Sb,As) and Ba2Ti2Fe2As3O

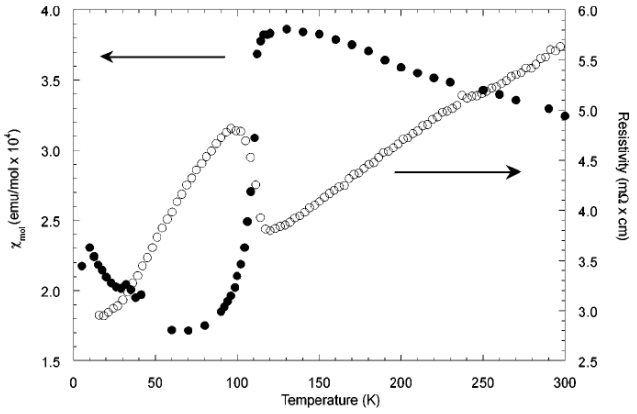
The Na2Ti2Sb2O was first synthesized by Adam and Schuster in 1990

A. Adam and H.-U.Z. Schuster, *Anorg. Allg. Chem.* **584**, 150 (1990)

Journal of Solid State Chemistry **153**, 275–281 (2000)

# Powder Neutron Diffraction Studies of $Na_2Ti_2Sb_2O$ and Its Structure–Property Relationships

Tadashi C. Ozawa, et al.




IG. 1. Temperature-dependent magnetism and electric resistivity of $Na_2Ti_2Sb_2O$ (Adapted from Ref. 12).

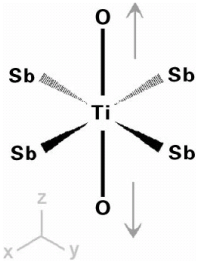
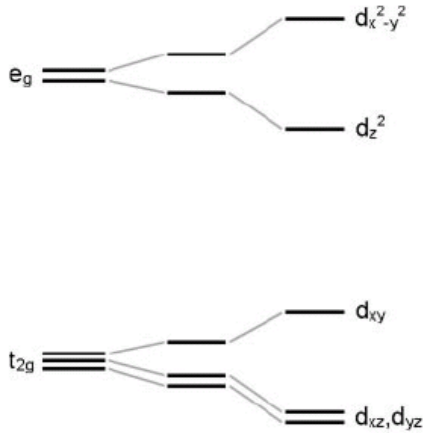



FIG. 5. Octahedral coordination of Ti with arrows showing the local distortion along O–Ti–O axis around the $T \approx 120$ K.



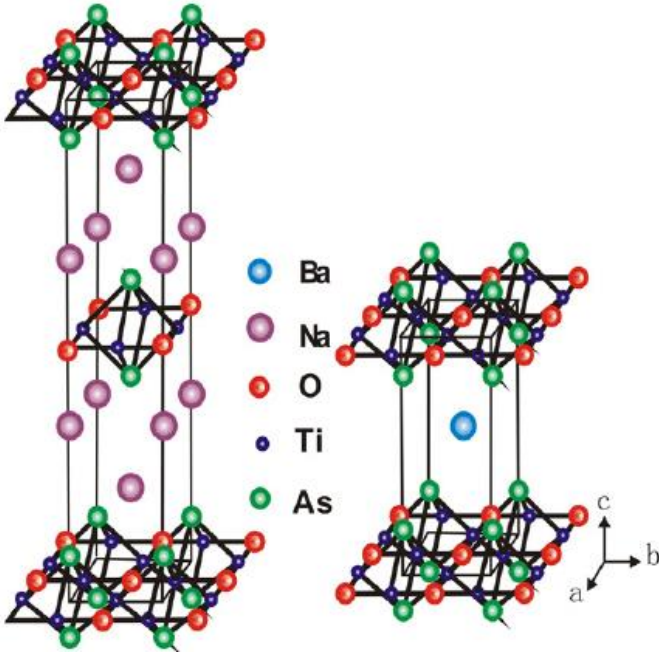

Small structure distortion,
No magnetic order observed!

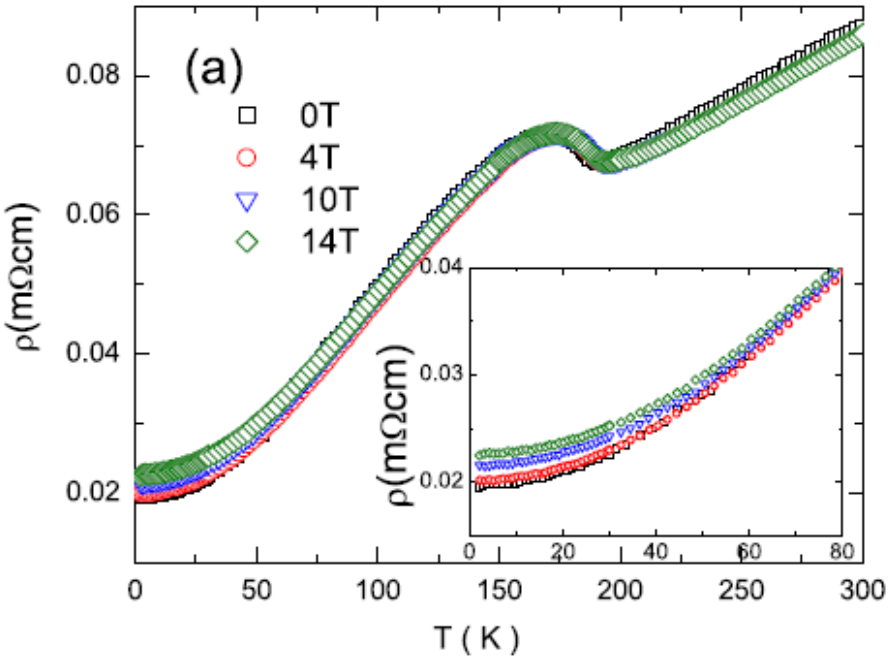
Quarter filled system

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **22** (2010) 075702 (5pp) doi:10.1088/0953-8984/22/7/075702

# Structure and physical properties for a new layered pnictide-oxide: $BaTi_2As_2O$

**X F Wang, Y J Yan, J J Ying, Q J Li, M Zhang, N Xu and X H Chen**[1]



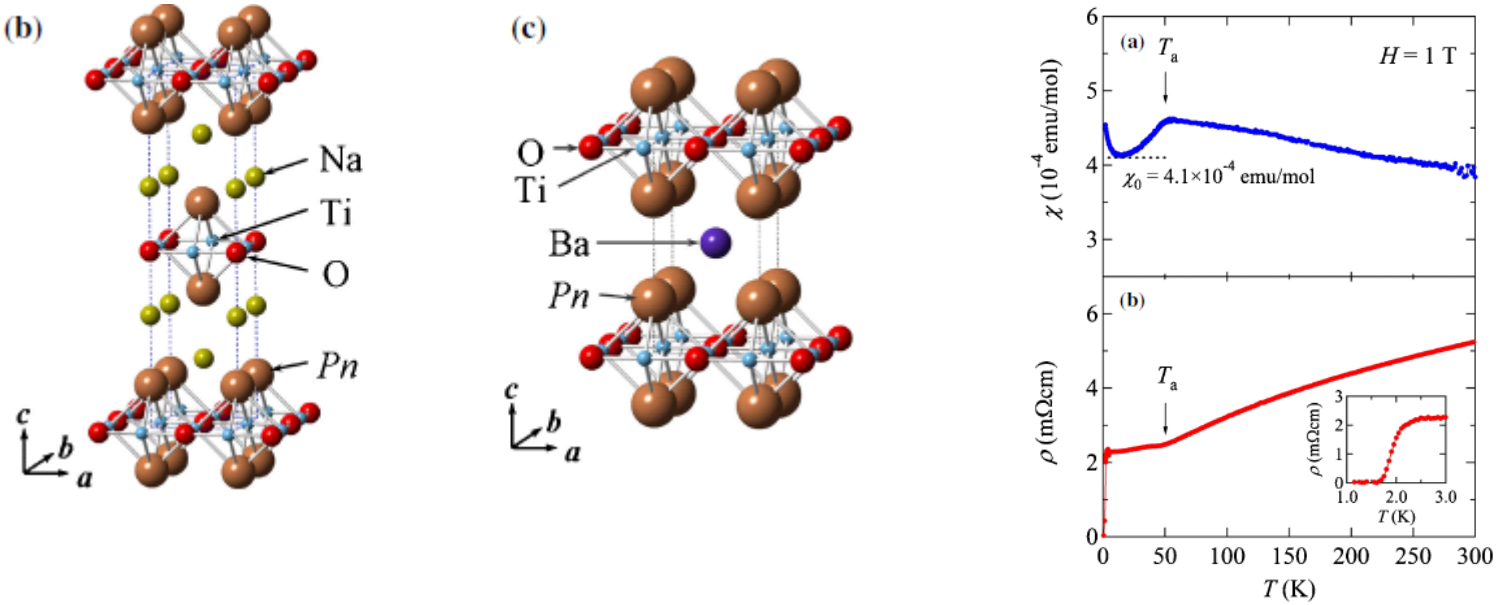
Journal of the Physical Society of Japan **81** (2012) 103706 LETTERS
http://dx.doi.org/10.1143/JPSJ.81.103706

# Superconductivity in $BaTi_2Sb_2O$ with a $d^1$ Square Lattice

Takeshi YAJIMA[1], Kousuke NAKANO[1], Fumitaka TAKEIRI[1], Toshio ONO[2], Yuko HOSOKOSHI[2], Yoshitaka MATSUSHITA[3], James HESTER[4], Yoji KOBAYASHI[1], and Hiroshi KAGEYAMA[1]

[1]*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan*
[2]*Department of Physical Science, Graduate School of Science, Osaka Prefecture University, Sakai 599-8531, Japan*
[3]*NIMS Beamline Station at SPring-8, National Institute for Materials Science, Sayo, Hyogo 679-5148, Japan*
[4]*Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia*

(Received July 25, 2012; accepted August 9, 2012; published online September 13, 2012)



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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY



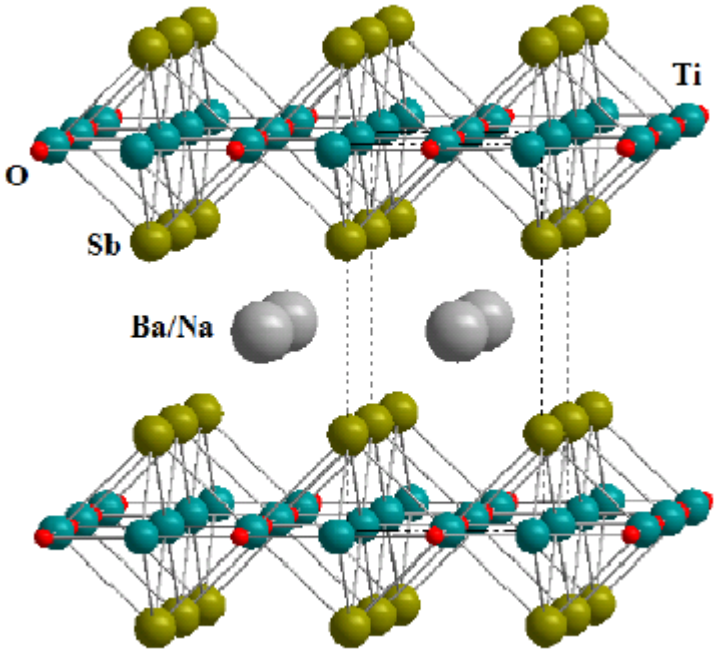
Communication

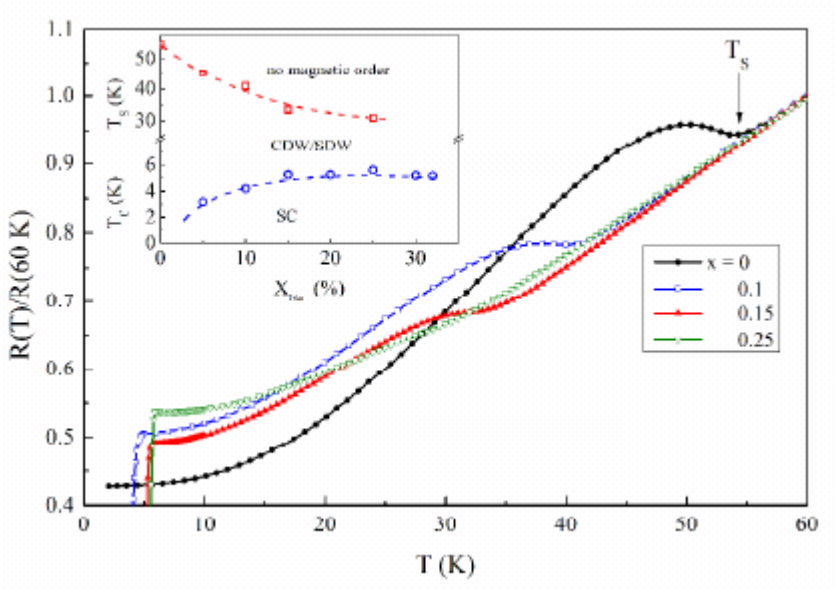
# Ba1-xNaxTi2Sb2O (0.0 # x# 0.33): A Layered Titanium-based Pnictide Oxide Superconductor.

Phuong Doan, Melissa Gooch, Zhongjia Tang, Bernd Lorenz, Angela Moeller, Joshua H. Tapp, Paul C.W. Chu, and Arnold Mejia Guloy

*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • Publication Date (Web): 21 Sep 2012

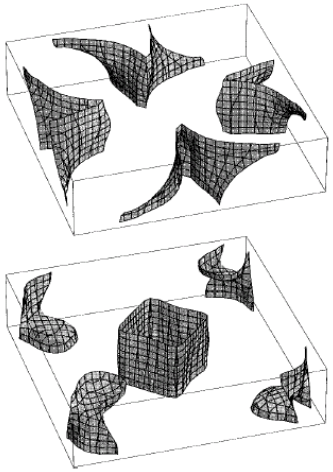




PHYSICAL REVIEW B VOLUME 58, NUMBER 8 15 AUGUST 1998-II

# Electronic instability in inverse-$K_2NiF_4$-structure $Na_2Sb_2Ti_2O$



W. E. Pickett
*Department of Physics, University of California–Davis, Davis, California 95616*
(Received 4 February 1998)

A square Fermi surface, nearly dispersionless in the $k_z$ direction, suggests a CDW or SDW that gaps this surface as the underlying cause of the transition. Without knowledge of

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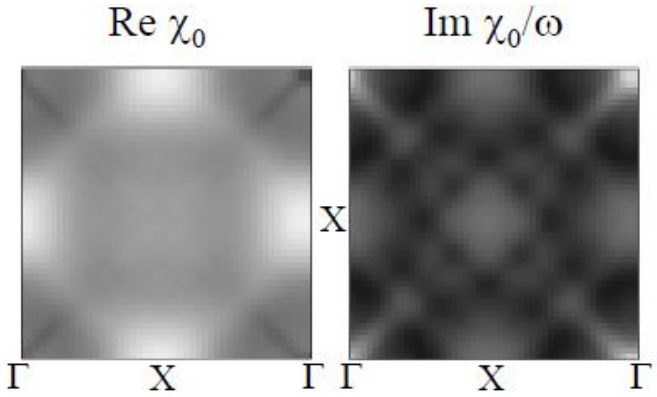
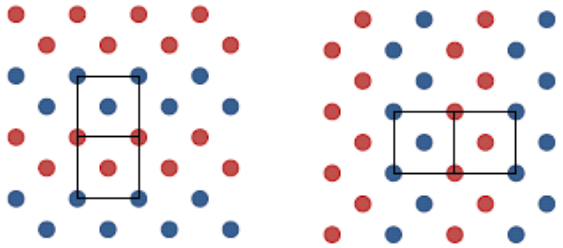
# Electronic structure, disconnected Fermi surfaces and antiferromagnetism in the layered pnictide superconductor $Na_xBa_{1-x}Ti_2Sb_2O$

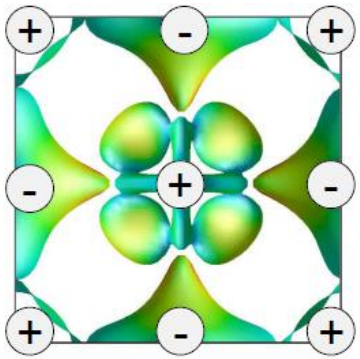
David J. Singh
*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056*
(Dated: September 24, 2012)




FS nesting



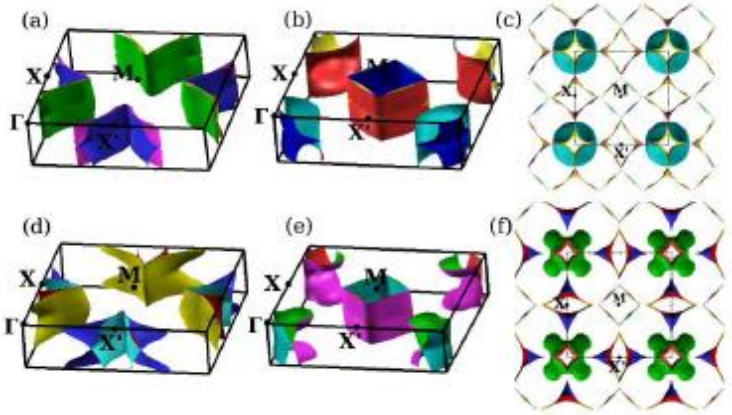
Bicollinear magnetic structure

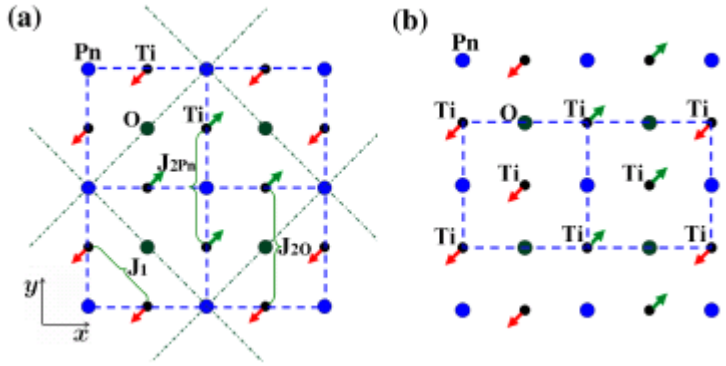



S+- pairing

# Layered pnictide-oxide $Na_2Ti_2Pn_2O$ (Pn=As, Sb): a paradigm for spin density waves

Xun-Wang Yan[1,2] and Zhong-Yi Lu[1*]
[1] *Department of Physics, Renmin University of China, Beijing 100872, China and*
[2] *School of Physics and Electrical Engineering, Anyang Normal University, Anyang 455002, China*
(Dated: October 15, 2012)




# Electron-phonon superconductivity and charge density wave instability in the layered titanium-based pnictide $Ba_{1-x}Na_xTi_2Sb_2O$

Alaska Subedi
*Centre de Physique Théorique, École Polytechnique, CNRS, 91128 Palaiseau Cedex, France*
(Dated: October 2, 2012)

I present the results of first principles calculations of the phonon dispersions and electron-phonon coupling for $BaTi_2Sb_2O$. The phonon dispersions show a weak lattice instability near the zone corners that leads to a CDW phase. The calculations of the electron-phonon coupling reveal strong coupling, especially to the in-plane Ti modes. The total coupling is large enough to readily explain the superconductivity in this compound. As the Fermi surfaces are disconnected with different orbital character weights, this compound is likely to host a multiband superconductivity. The role of spin fluctuations in suppressing the superconducting $T_c$ is also discussed.

# A site-selective antiferromagnetic ground state in layered pnictide-oxide $BaTi_2As_2O$

Xiang-Long Yu,[1,2] Da-Yong Liu,[1] Ya-Min Quan,[1] Ting Jia,[1] Hai-Qing Lin,[3] and Liang-Jian Zou[1, a)]
[1)] *Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P. O. Box 1129, Hefei 230031, China*
[2)] *University of Chinese Academy of Sciences, Beijing 100000, China*
[3)] *Beijing Computational Science Research Center, Beijing 100084, China*

The electronic and magnetic properties of $BaTi_2As_2O$ have been investigated using both the first-principles and analytical methods. The full-potential linearized augmented plane-wave calculations show that the most stable state is a site-selective antiferromagnetic (AFM) metal with a $2 \times 1 \times 1$ magnetic unit cell containing two nonmagnetic Ti atoms and two other Ti atoms with antiparallel moments. Further analysis to Fermi surface and spin susceptibility shows that the site-selective AFM ground state is driven by the Fermi surface nesting and the Coulomb correlation. Meanwhile, the charge density distribution remains uniform, suggesting that the phase transition at 200 K in experiment is a spin-density-wave (SDW) transition.

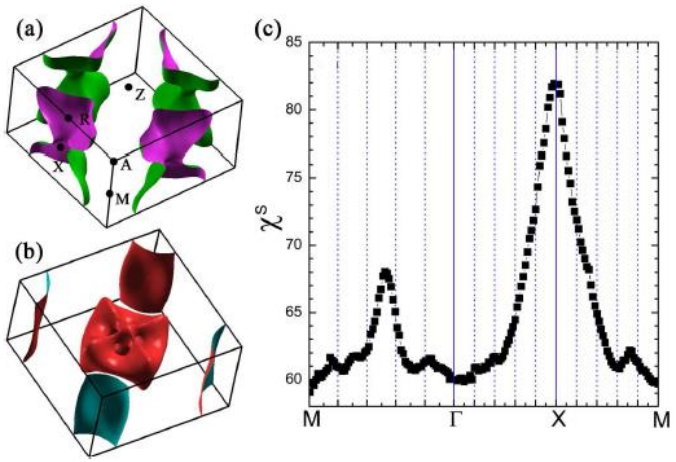
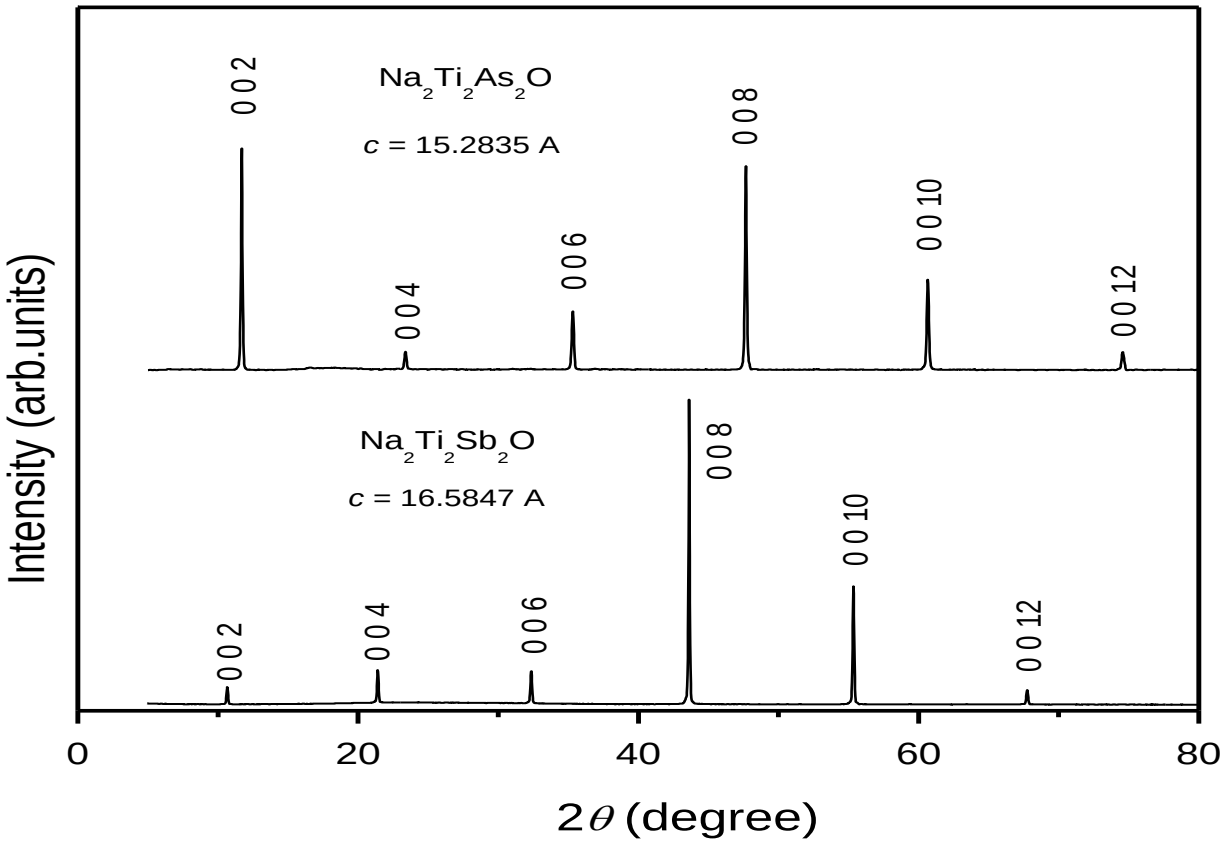


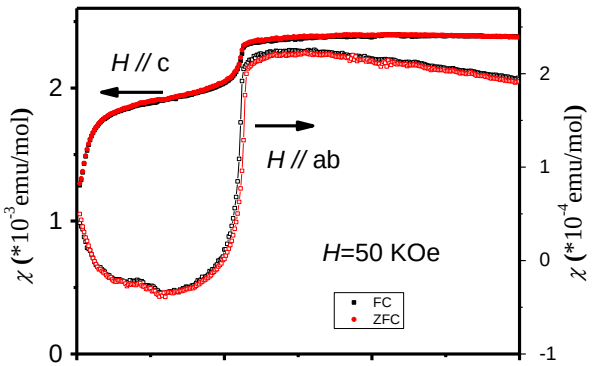

FIG. 2. (Color online) Fermi surfaces and spin susceptibility of $BaTi_2As_2O$ in NM state within the GGA sheme: (a) hole-type Fermi surface sheets, (b) electron-type Fermi surface sheets and (c) the real part of $\chi^S$ with arbitrary unit.

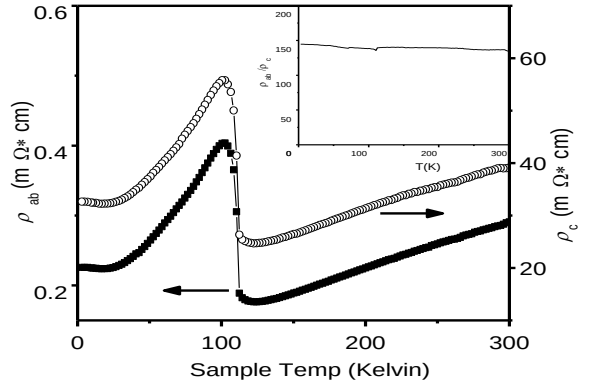
arXiv:1402.4723

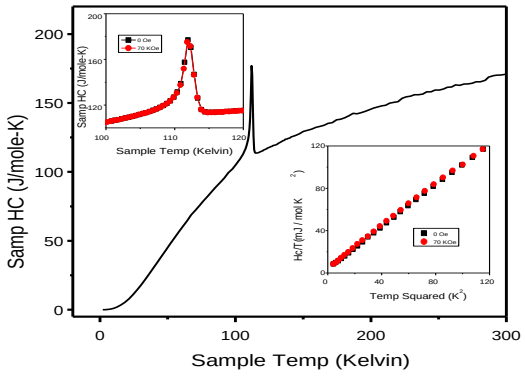
# We grew single crystals of Na2Ti2Pn2O (Pn=Sb, As) by flux method



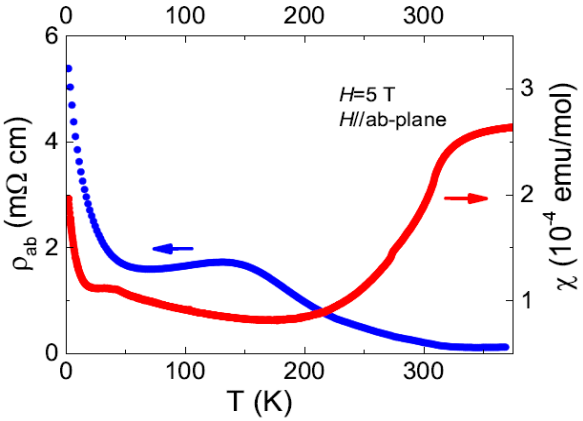
# Na2Ti2Sb2O

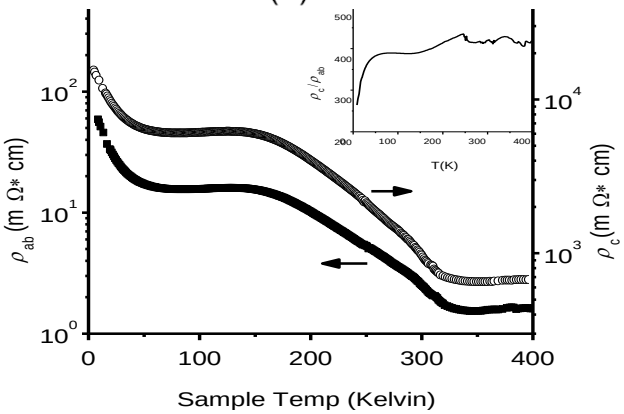


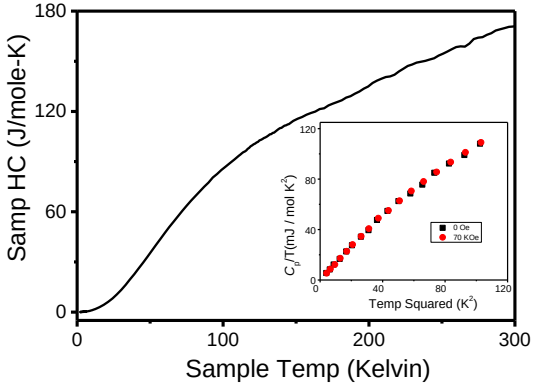




# Na2Ti2As2O

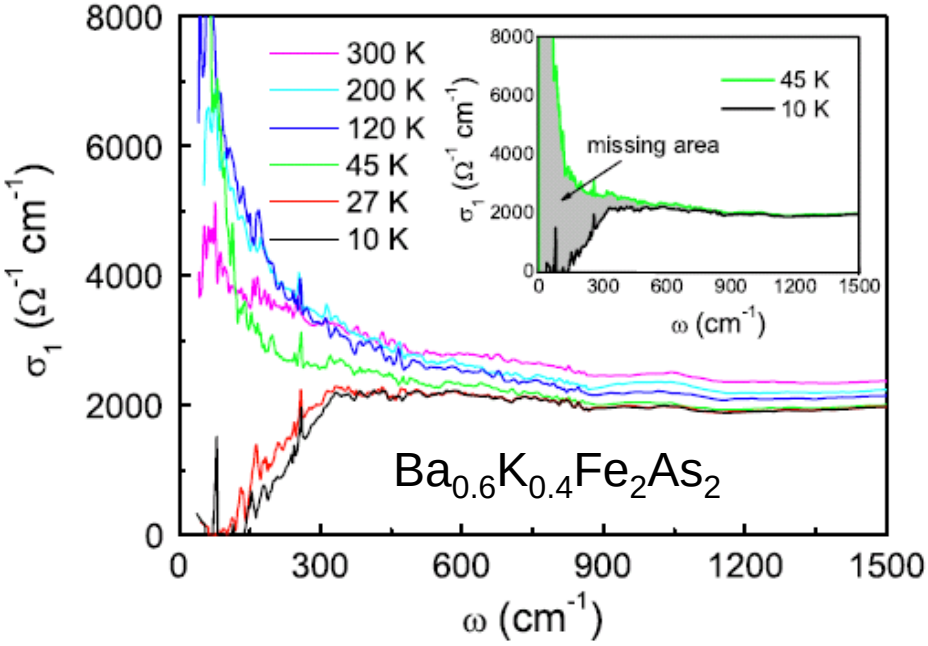


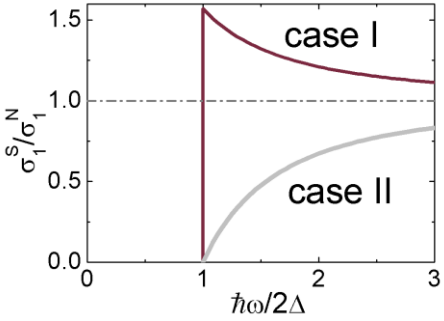




Anisotropic resistivity measured by Montegomery method

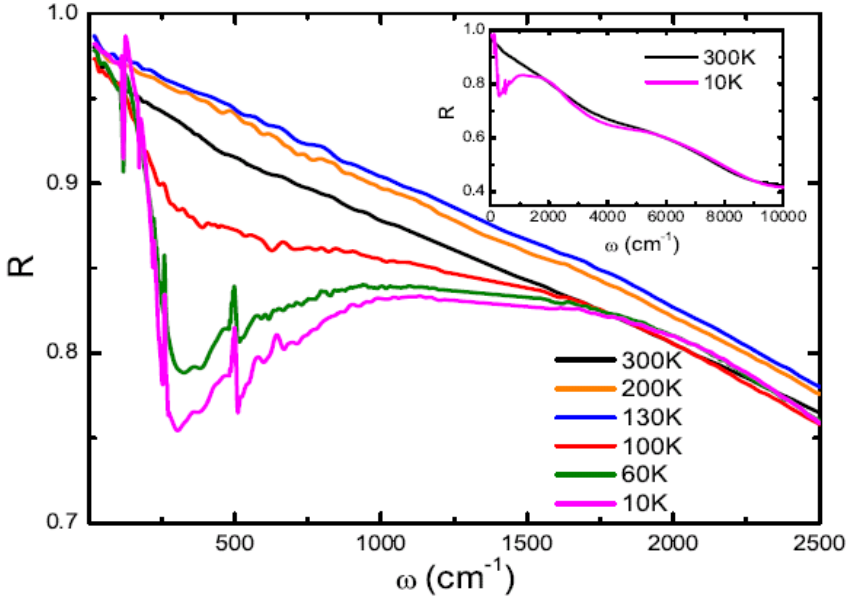
Y. G. Shi et al. PRB 88, 144513 (2013)

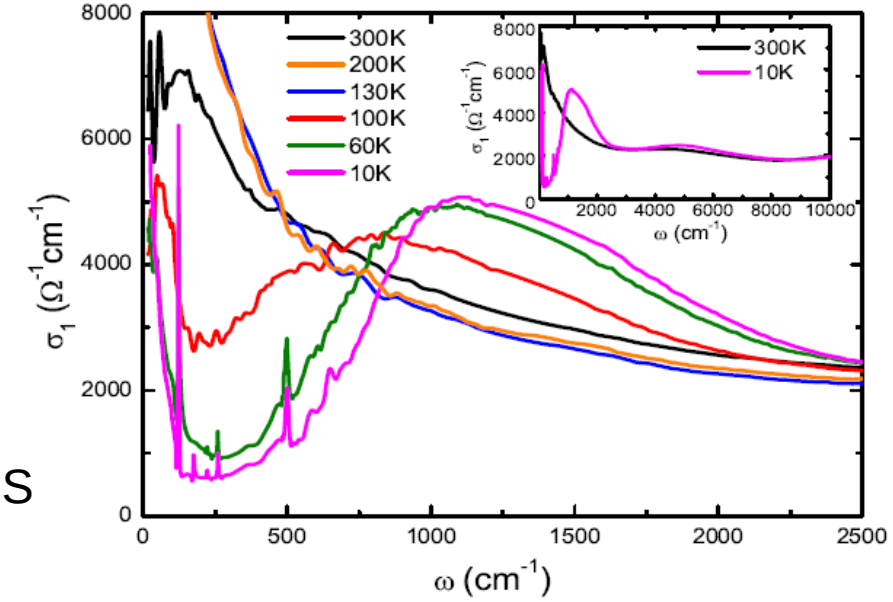


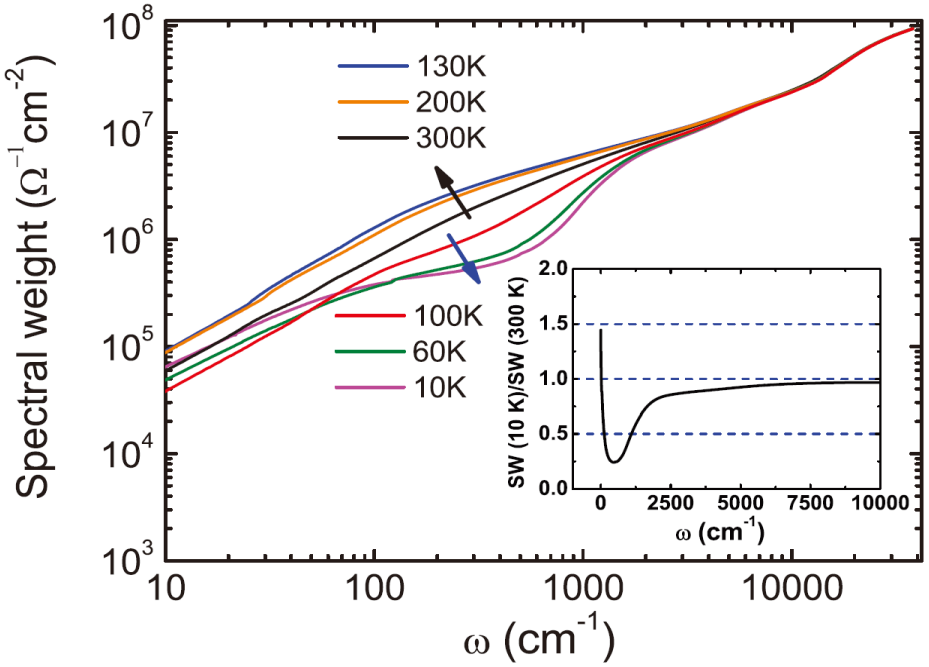



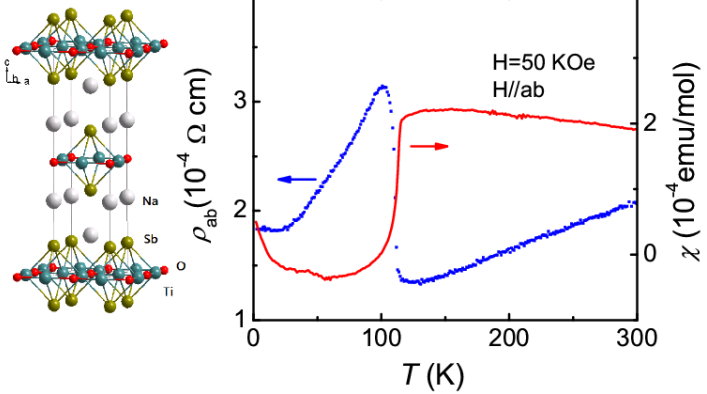

$$2\Delta/k_BT_s \approx 14$$

Much larger than the mean field value of BCS theory. Strong fluctuation effect due to 2D?

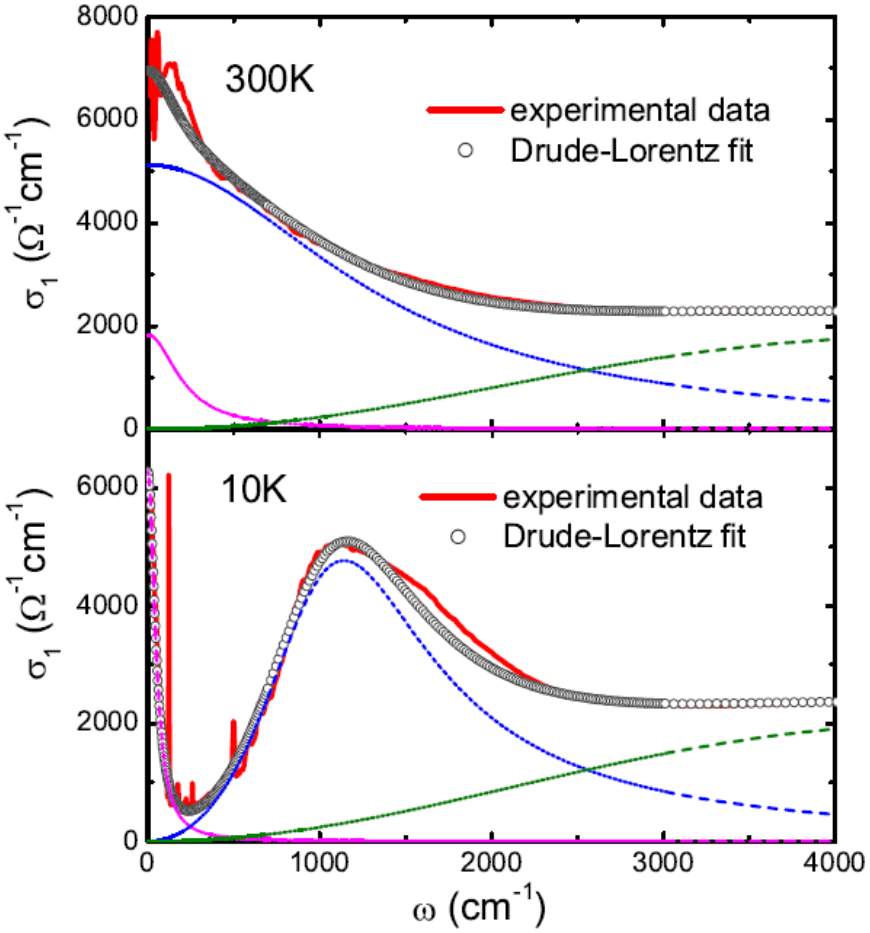





Gapped feature in spectral weight analysis




$$\omega_p = (\omega_{p1}^2 + \omega_{p2}^2)^{1/2}$$

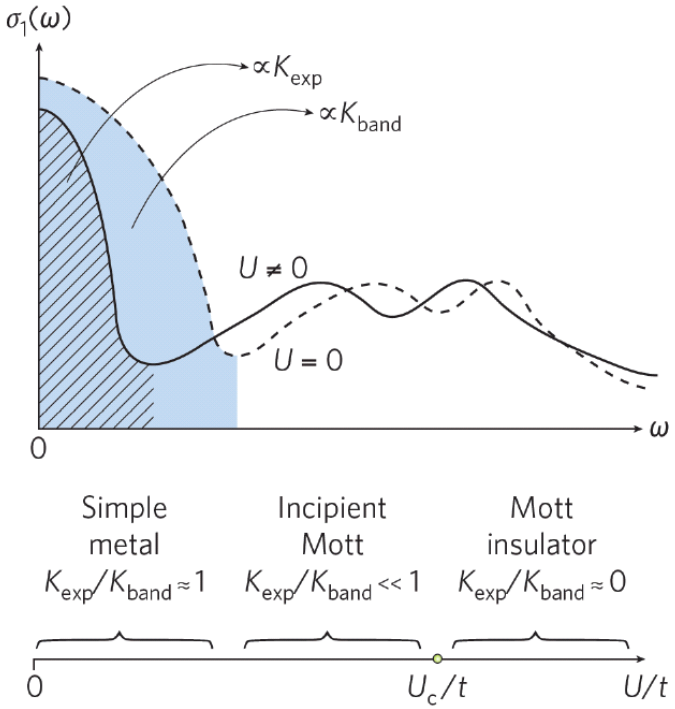
or $\omega_p^2 = 8\int_0^{\omega_c} \sigma_1(\omega) d\omega$

$\omega_p \approx 20000$ cm$^{-1}$ (2.5 eV) at 300 K

$\omega_p \approx 4300$ cm$^{-1}$ (0.53 eV) at 10 K

**Over 95% of free carrier spectral weight was gapped away.**

$$\epsilon(\omega) = \epsilon_\infty - \sum_i \frac{\omega_{p,i}^2}{\omega_i^2 + i\omega/\tau_i} + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\omega/\tau_j}$$




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

Q M Si, Nature Physics 2009

$$K_{exp}/K_{band} = \omega^2_{p,exp}/\omega^2_{p,band}$$

Experiment:

$\omega_p \approx 20000$ cm$^{-1}$ (2.5 eV) at 300 K

Band structure calculation:
$\omega_p \approx 3$ eV (W. Pickett, PRB 98)

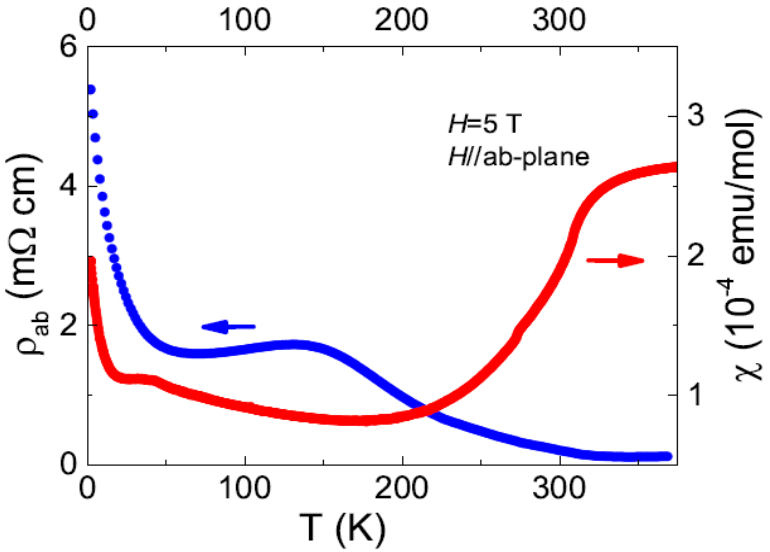
**$K_{exp}/K_{band}$~0.7, weak correlation effect**

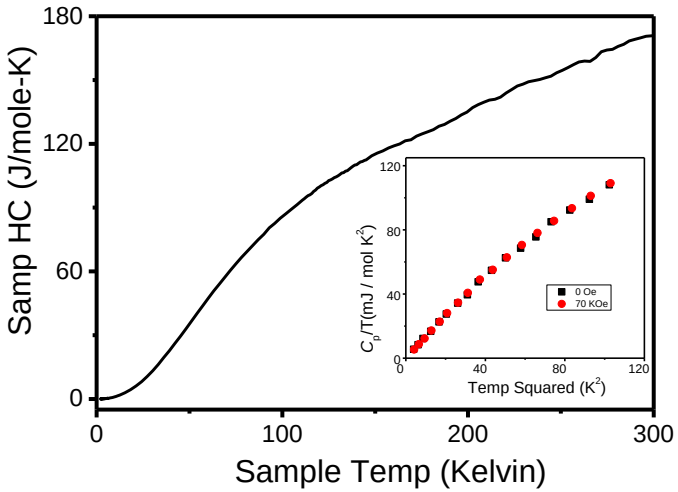
# Summary of Na2Ti2Sb2O

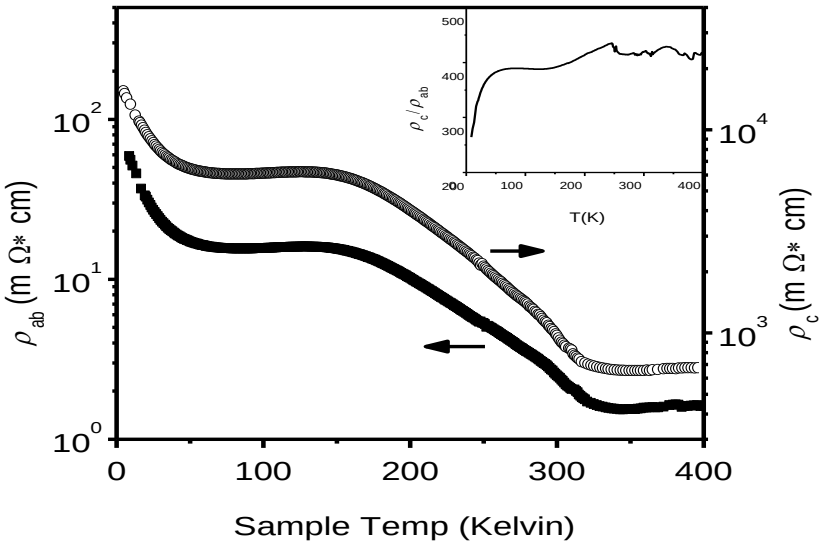
- The optical study revealed dramatic spectral change across the phase transition at 114 K and formation of a density-wave energy gap at low T.
- The opening of the gap removes most part of the free carrier spectral weight and causes a substantial reduction of the carrier scattering rate.
- The ratio of $2\Delta/k_BT_s$~14, suggesting that the transition temperature is significantly lower than the mean-field transition temperature.
- A weak correlation effect in the titanium oxypnictides.

Y. Huang et al.,Phys. Rev. B 87, 100507 (R) (2013)

# Na2Ti2As2O single crystal



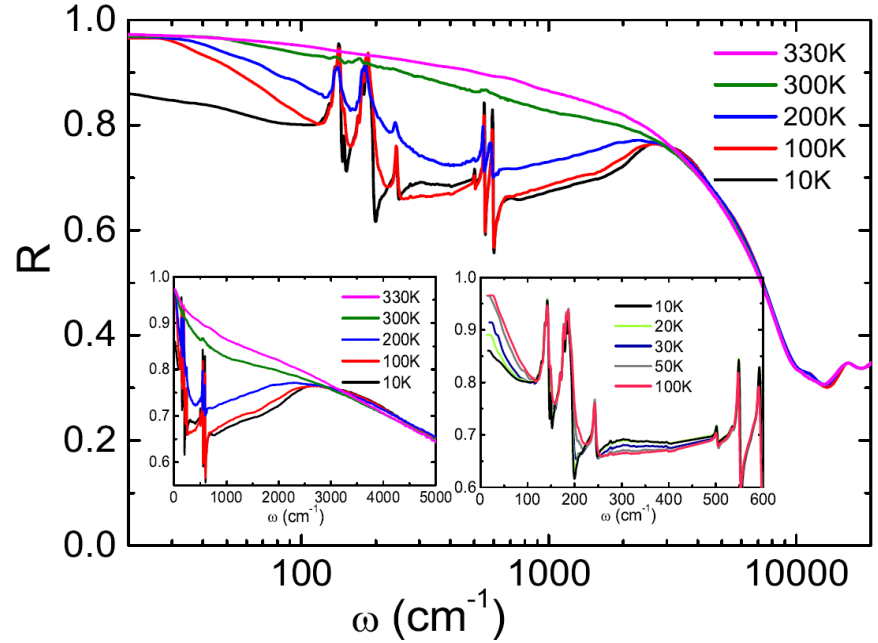



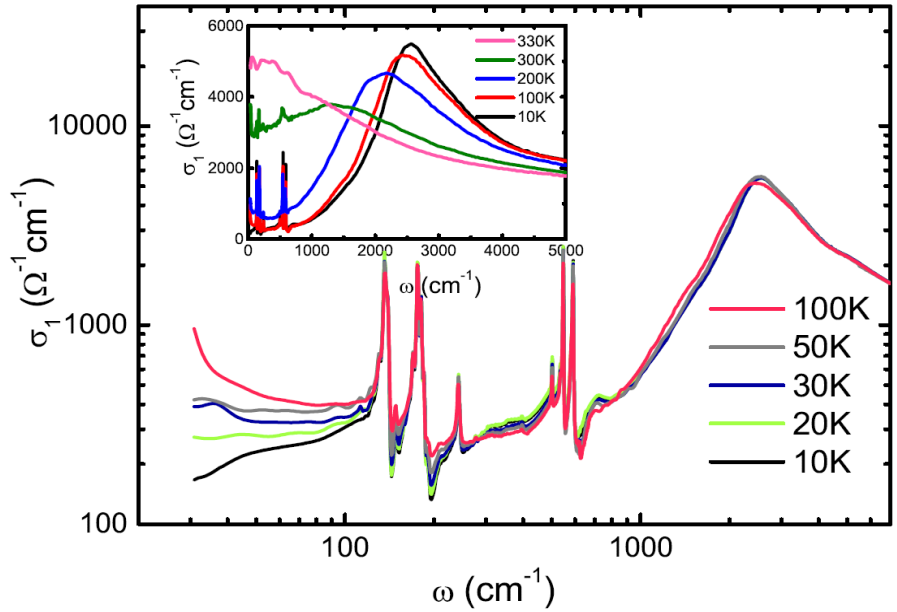




Anisotropic resistivity measured by Montegomery method

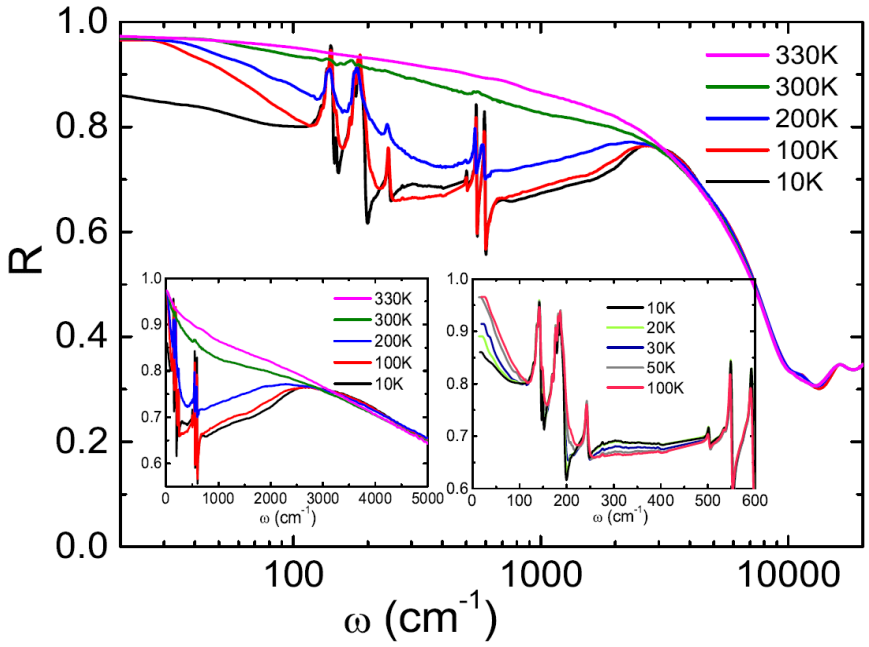
Y. G. Shi et al. PRB 88, 144513 (2013)

# Na2Ti2As2O

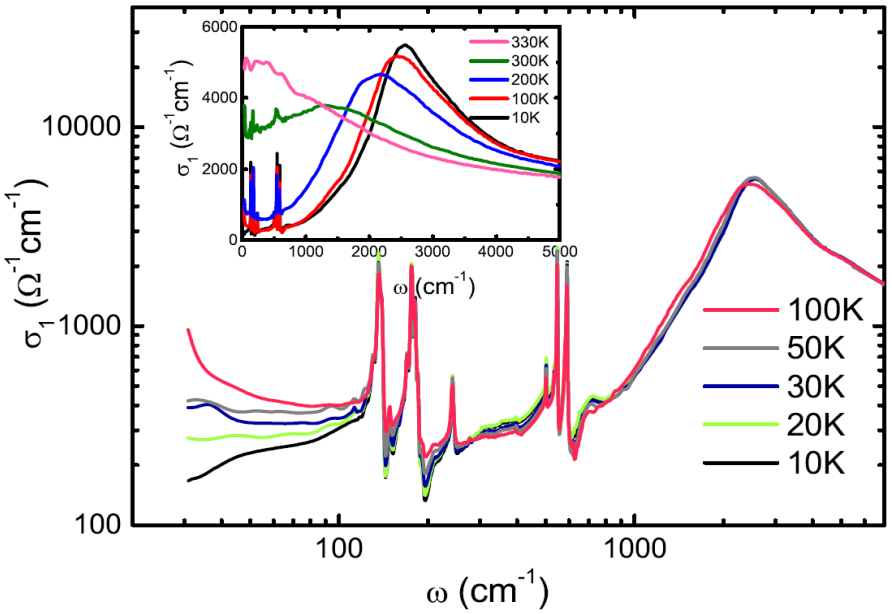


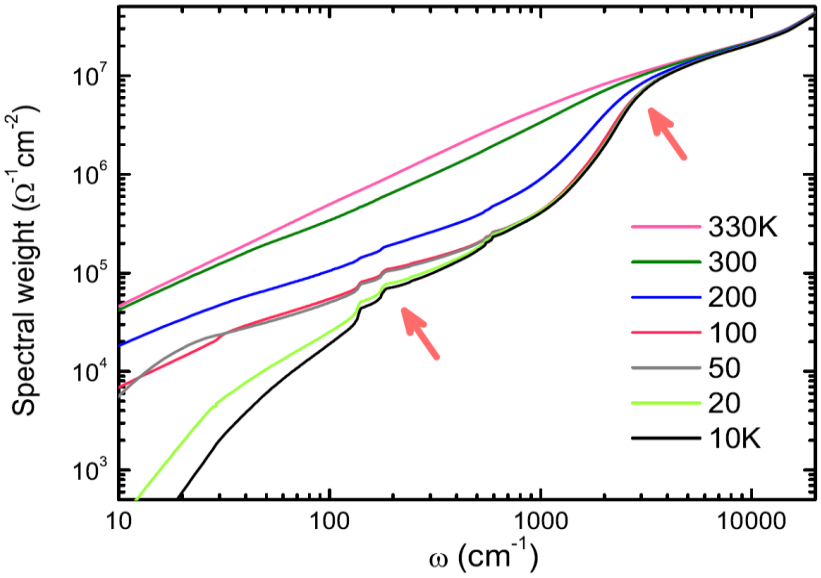




- Formation of partial density wave energy gap below 320 K;
- Still metallic below 320 K;
- Substantial reduction of both free carrier spectral weight and scattering rate;



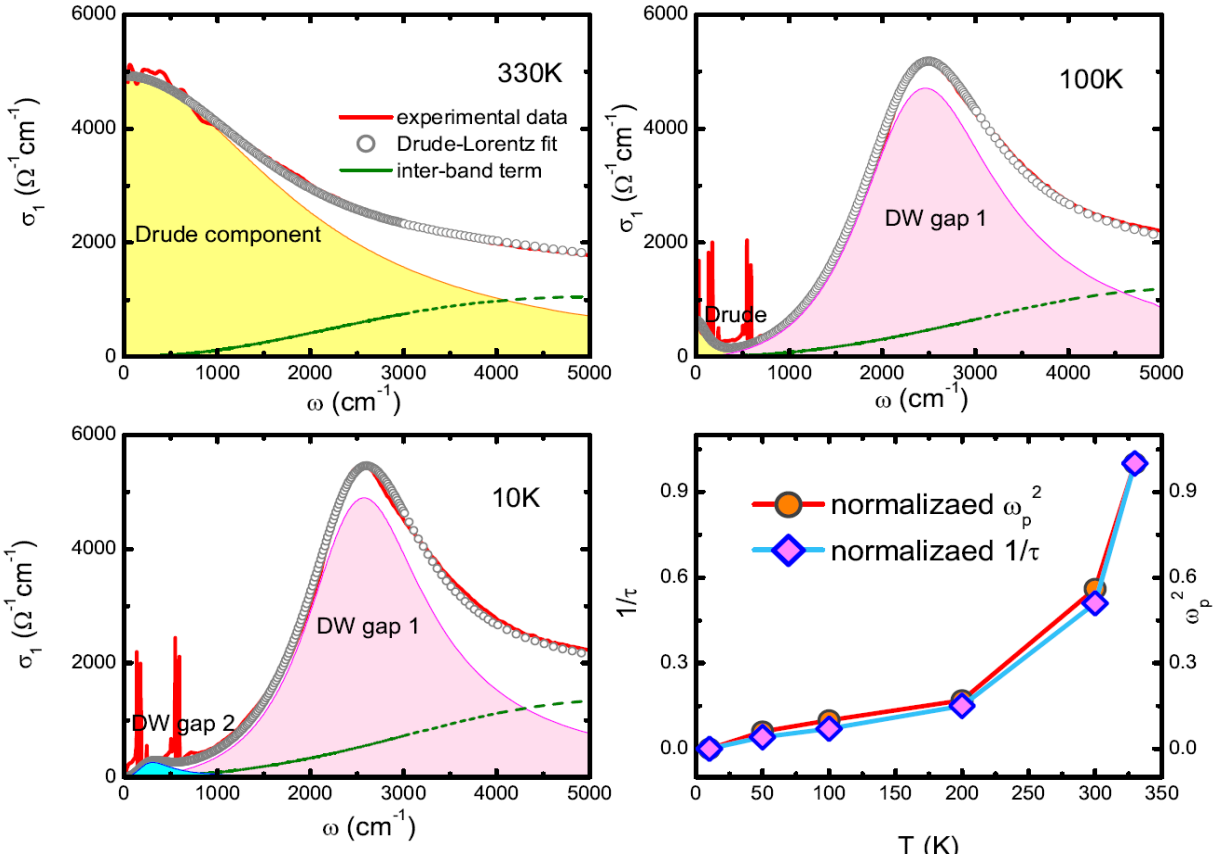

- Another density wave gap structure forms below 40 K, resulting in an insulating ground state




$$2\Delta_2/k_BT_2 \sim 10$$

for small gap near 220 cm-1




- Substantial reduction of both free carrier spectral weight and scattering rate;

$$2\Delta = 2600\ \mathrm{cm}^{-1}\ (\sim 0.32eV)$$

$$2\Delta / k_B T_s \approx 11.5$$

# Several remarks:

1. 2D insulator driven by DW phase transition—a rare case! DFT calculations on Na2Ti2As2O indeed predicted an insulating ground state, but the calculations did not consider two steps phase transitions. A more realistic approach to the ground state is to consider first a metastable intermediate DW state (which might be CDW), then examine further possible instability (CDW or SDW) on the basis of this intermediate state.

2. Although the optical measurement revealed formation of two energy gaps at different temperatures, the measurement could not determine where the FSs are gapped. Momentum resolved experimental probe, such as ARPES, should be used to determine the gapped regions and corresponding wave vectors.

3. Optical measurement can not tell whether the phase transitions are CDW or SDW, since both orders have the same coherent factor. Other techniques which are capable to probe magnetic order should be used to resolve the issue

A recent NMR measurement by Kitagawa et al. on BaTi2Sb2O polycrystalline sample revealed an absence of internal field at the Sb site, which therefore favored an CDW origin. It is consistent with DFT calculations on BaTi2Sb2O.

But for Na2Ti2As2O, an SDW was predicted by DFT.

Y. Huang et al. PRB 89, 155120 (2014)

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Communication
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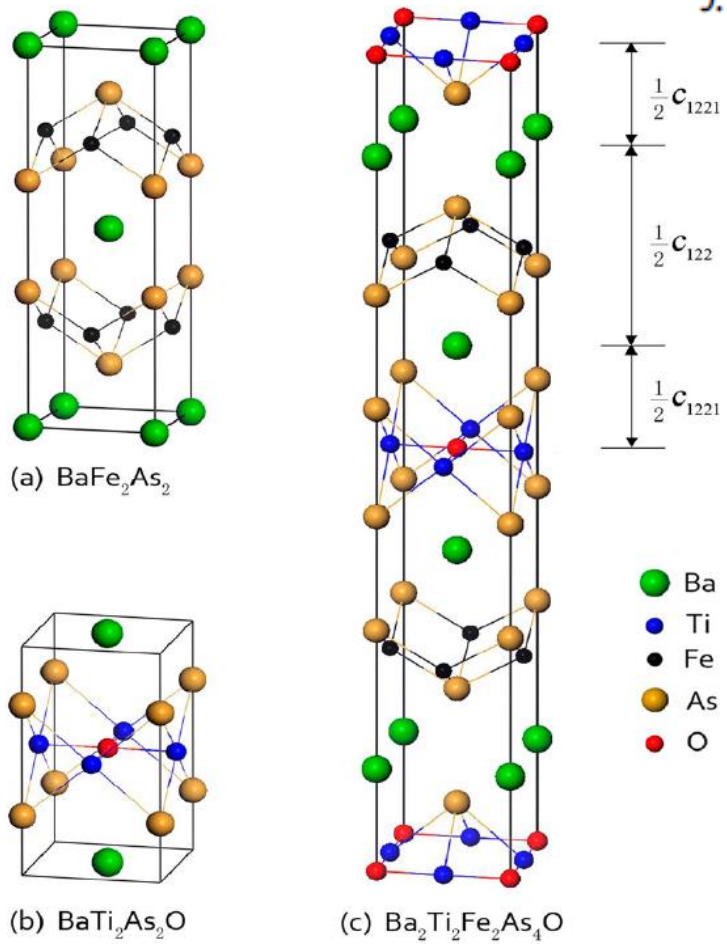
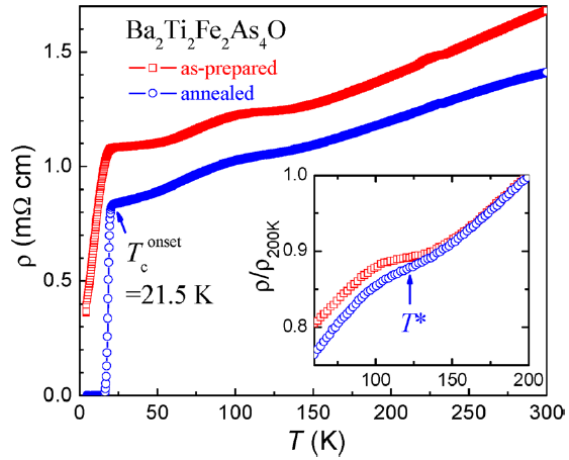
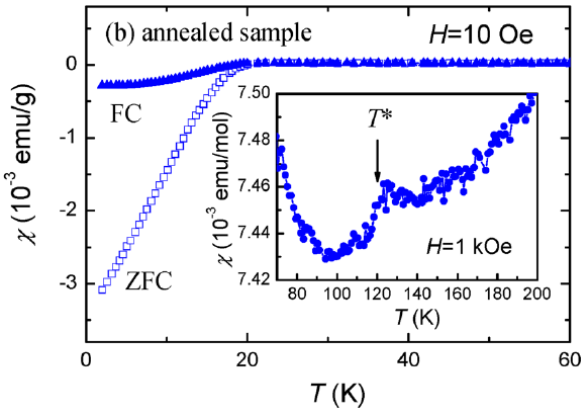
# $Ba_2Ti_2Fe_2As_4O$: A New Superconductor Containing $Fe_2As_2$ Layers and $Ti_2O$ Sheets

Yun-Lei Sun,[†] Hao Jiang,[†] Hui-Fei Zhai,[†] Jin-Ke Bao,[†] Wen-He Jiao,[†] Qian Tao,[†] Chen-Yi Shen,[†] Yue-Wu Zeng,[§] Zhu-An Xu,[†,‡] and Guang-Han Cao*[,†,‡]

J. Am. Chem. Soc. 2012, 134, 12893−12896



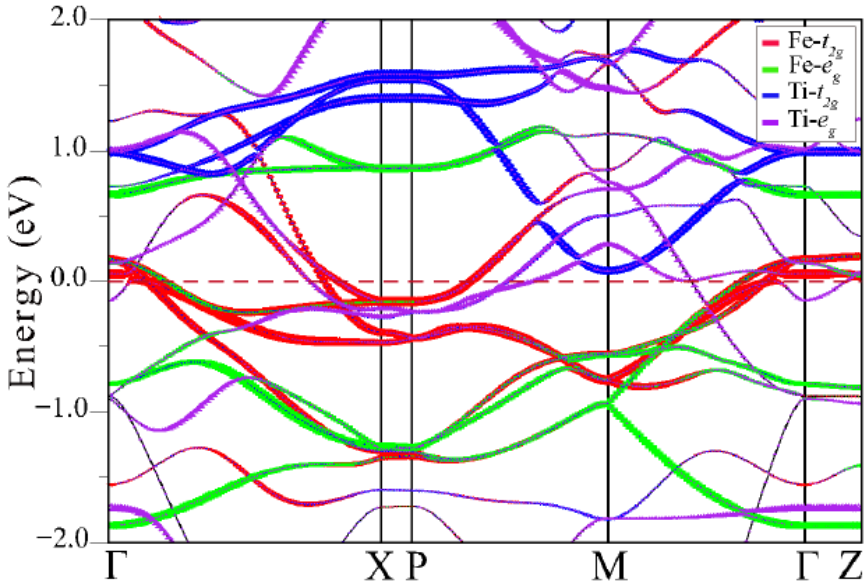
# Self-doping effect and possible antiferromagnetism at titanium-layers in the iron-based superconductor $Ba_2Ti_2Fe_2As_4O$

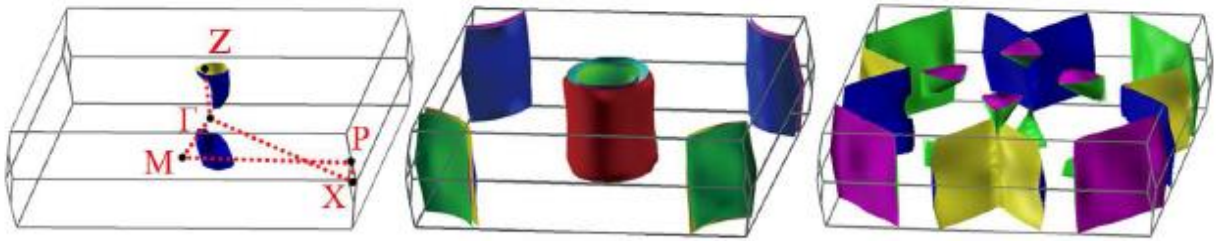
Hao Jiang,[1] Yun-Lei Sun,[1] Jianhui Dai,[2] Guang-Han Cao,[1,*] and Chao Cao[2,†]

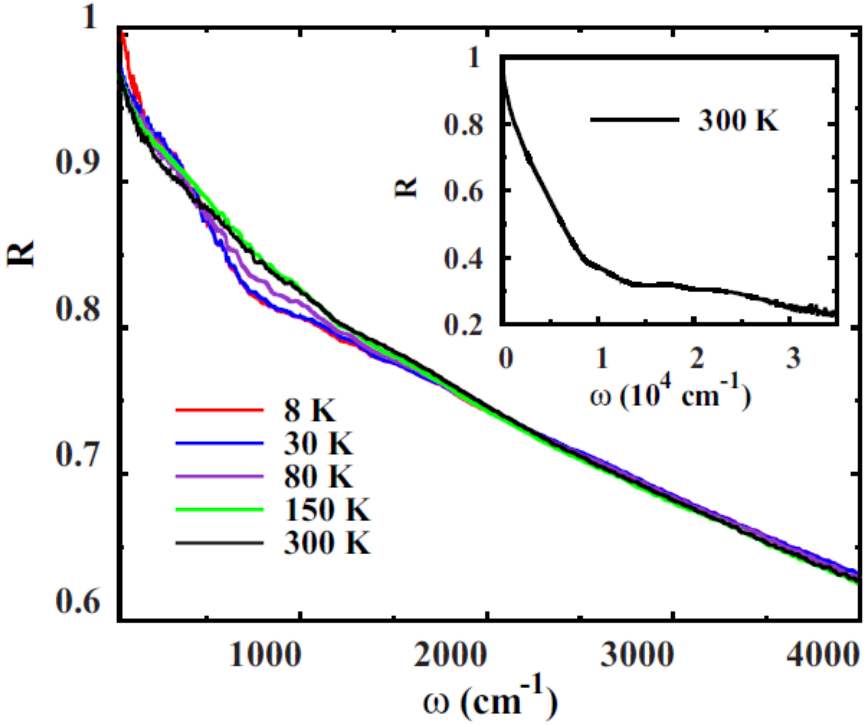
[1] *Department of Physics, State Key Lab of Silicon Materials, and Center for Correlated Matter, Zhejiang University, Hangzhou 310027, China*

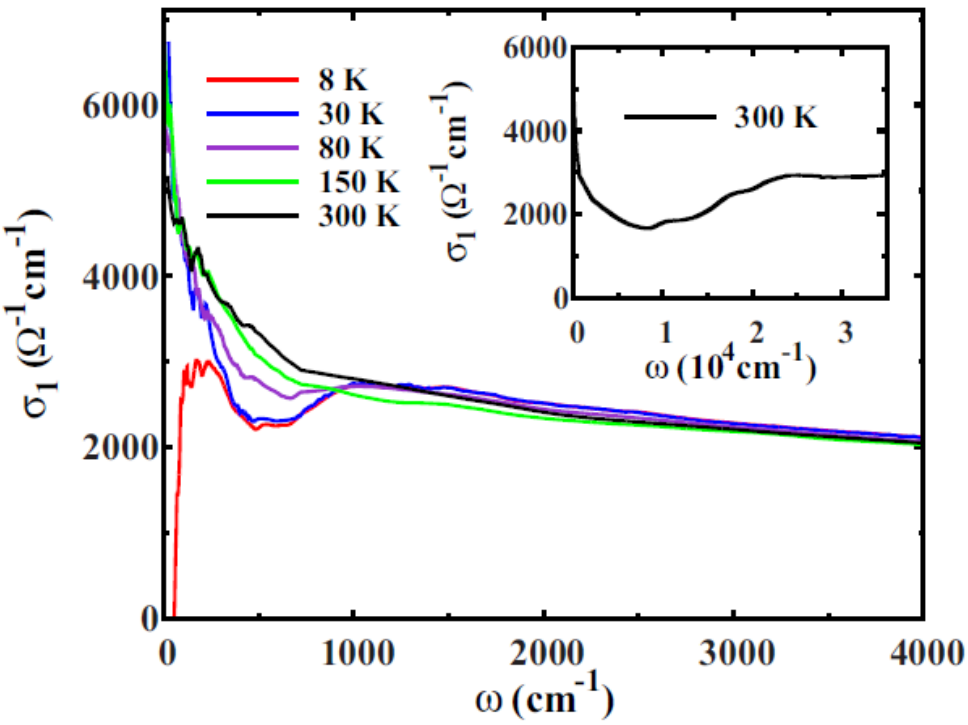
[2] *Condensed Matter Physics Group, Department of Physics, Hangzhou Normal University, Hangzhou 310036, China*

(Dated: July 31, 2012)

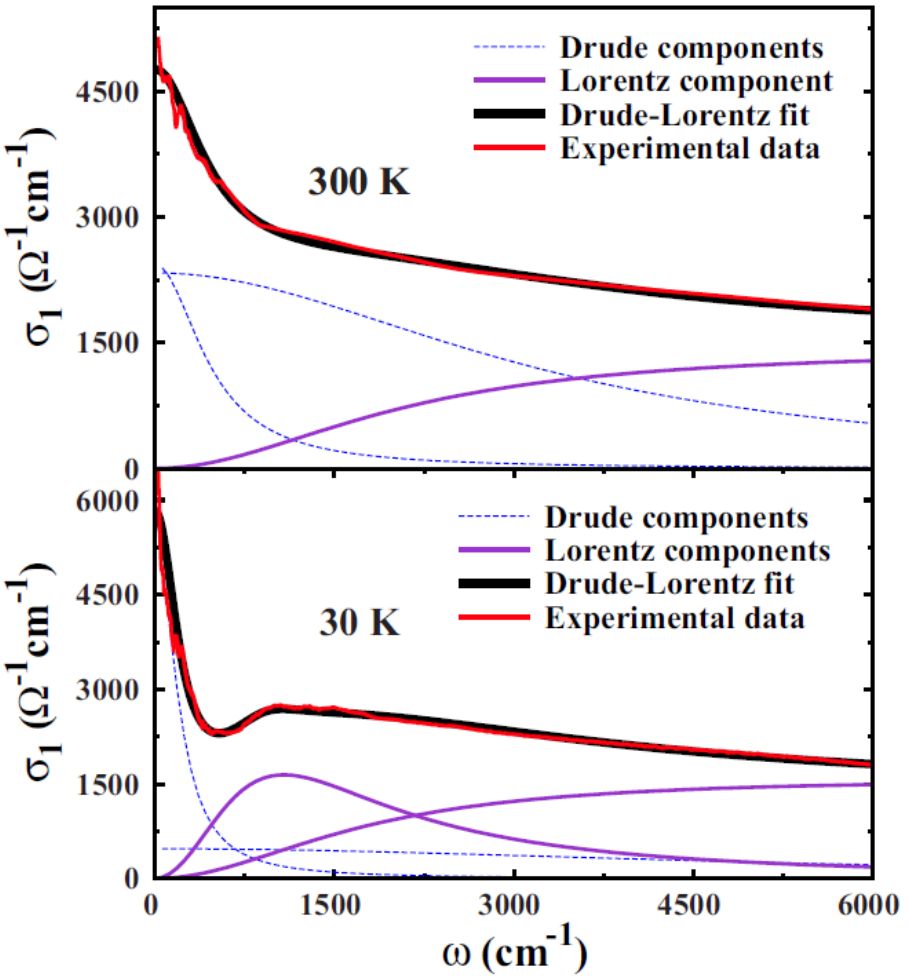



R
ω (cm-1)
8 K
30 K
80 K
150 K
300 K
300 K
ω (10^4 cm^-1)


σ1 (Ω-1cm-1)
ω (cm-1)
8 K
30 K
80 K
150 K
300 K
300 K
ω (10^4cm^-1)

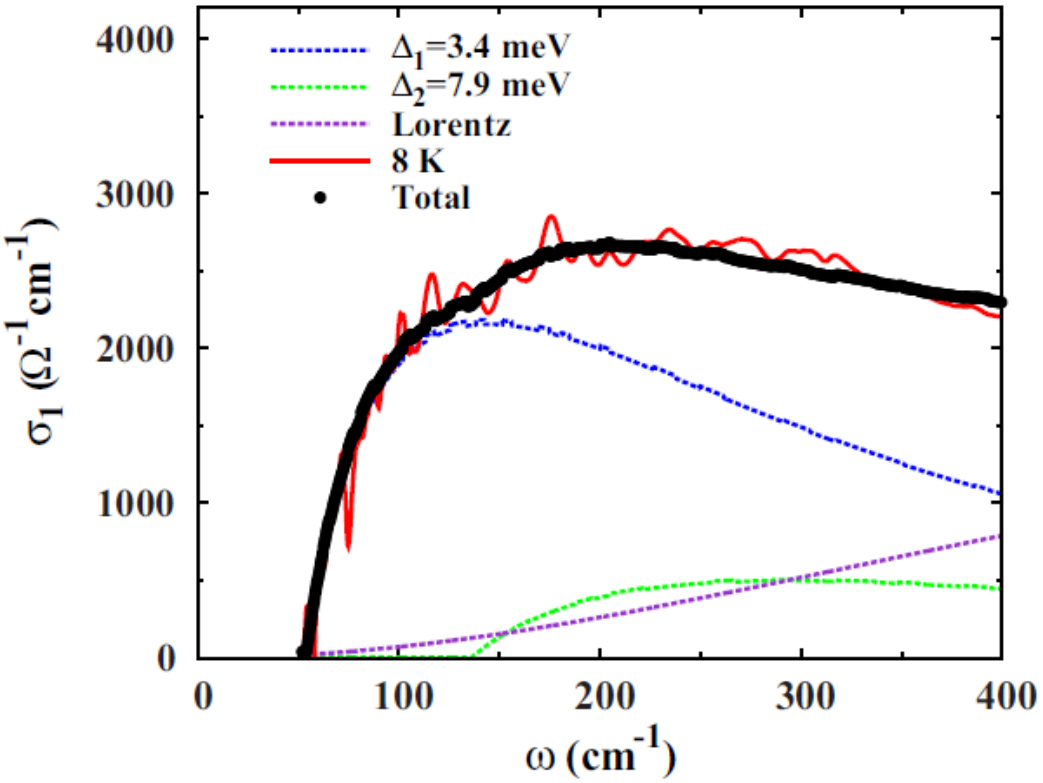
# DW state




The overall plasma frequency $\omega_p$ is considered to contribute from two different channels with $\omega_p = (\omega_{p1}^2 + \omega_{p2}^2)^{1/2}$. In the present case we obtain $\omega_p \approx 21\,600$ cm$^{-1}$ above $T_{DW}$ and $\omega_p \approx 15\,000$ cm$^{-1}$ at 30 K. Another method to estimate the

$$\omega_{p,30k}^2 / \omega_{p,300k}^2 \approx 48\%$$

# SC state




$$\Delta_1 = 3.4\,\text{meV}, 1/\tau_1 = 10\Delta_0 \text{ and } \Delta_2 = 7.9\,\text{meV}, 1/\tau_2 = 6\Delta_0$$

$$W_c \equiv W_s(\omega_c, T \approx T_c) - W_s(\omega_c, T \ll T_c) = \omega_{p,S}^2/8 \Rightarrow \lambda \approx 2900\ \text{Å}$$

H. P. Wang et al. PRB 90, 144508 (2014)
(Editor's suggestion)

Thank you!