The curious case of NiS:

Is it a metal or is it not?!

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Bad metal behavior in Mott systems

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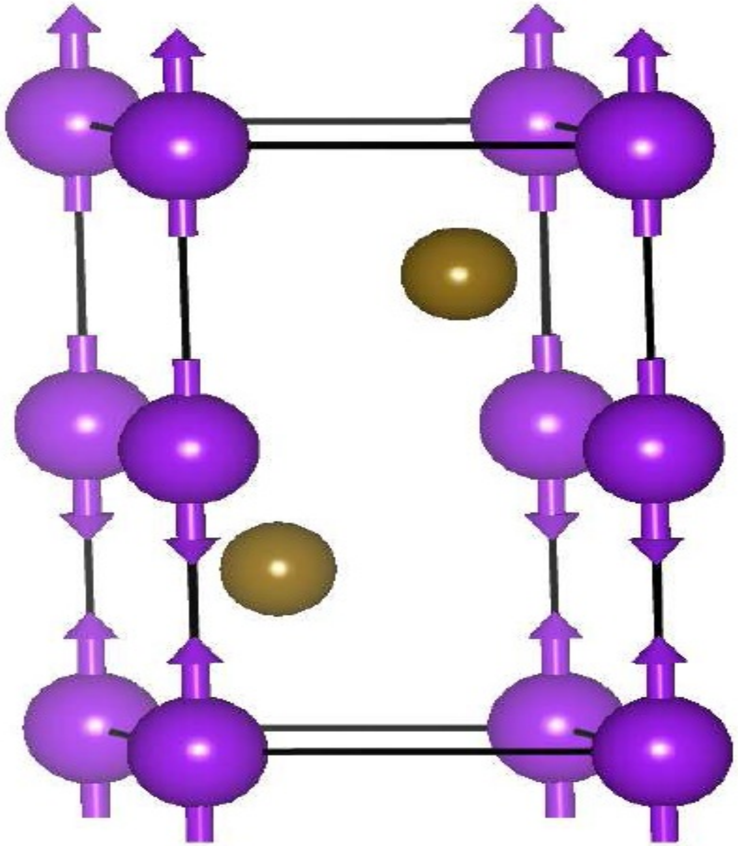
Crystal Structure and phase transition



- NiS forms in the hexagonal NiAs Structure. Ni atoms are in the octahedra of S atoms.

- It undergoes a first order phase transition between antiferromagnetic to paramagnetic state at 263K.

  Sparks *et al*, JAP 34,1191(1963)

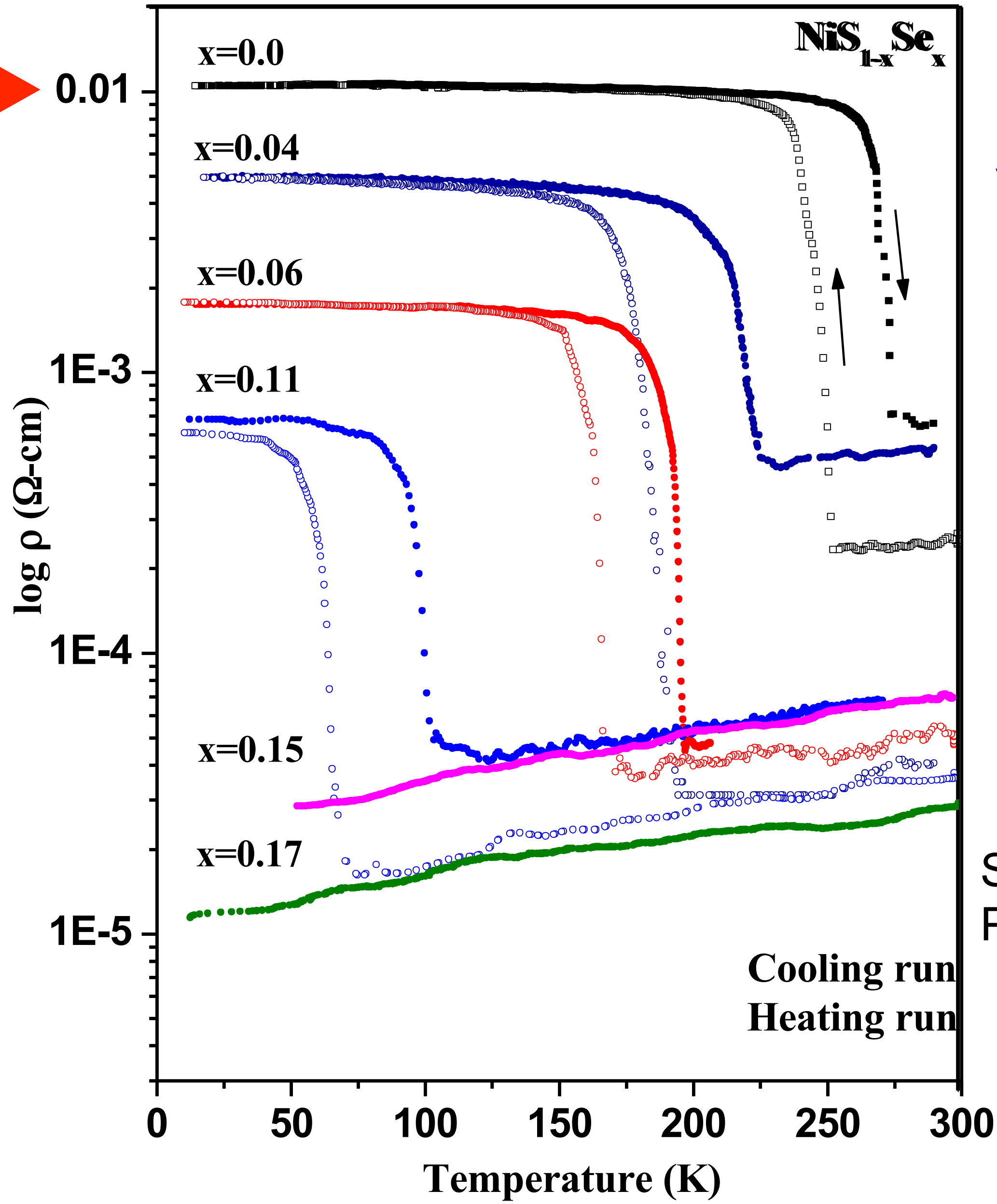
- At the transition temperature (T_t), hexagonal lattice parameters 'a' and 'c' increase in going from high to low temperature phase.

  Trahan *et al* PRB,2,2859(1970)

- All the Ni atoms are ferro-magnetically coupled within the *ab* plane and antiferromagnetically coupled along the c axis.
- In the low temperature phase magnetic moment/Ni=1.45 μ_B

Coey *et al*, PRL,32,1257(1974)

Curious aspects: (i) Transport



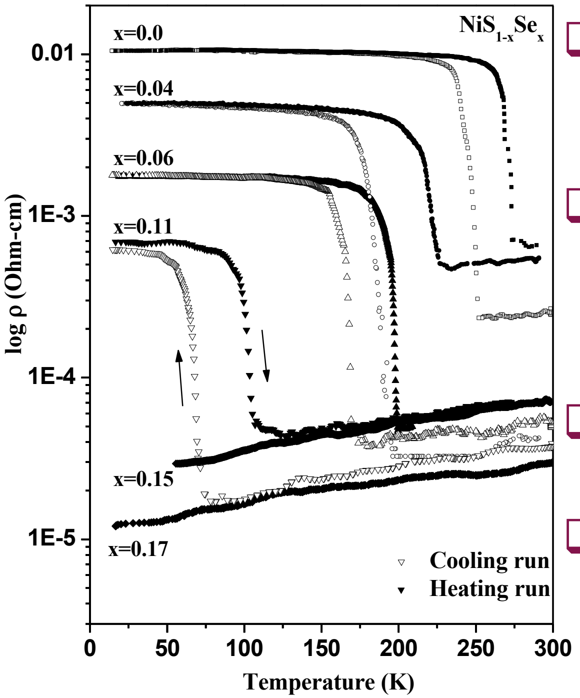
$\rho(T) = \rho_0$ + A T + B T²

Very bad!

Bad

S. R. Krishnakumar, Ph.D. Thesis

Resistivity and (ii) Hall Coefficient



- Below T_t ~ 10^{-3} Ω-c of the ord
- Resistivit constant range, 4-
- Above T_t decrease
- Type of t changes i temp pha

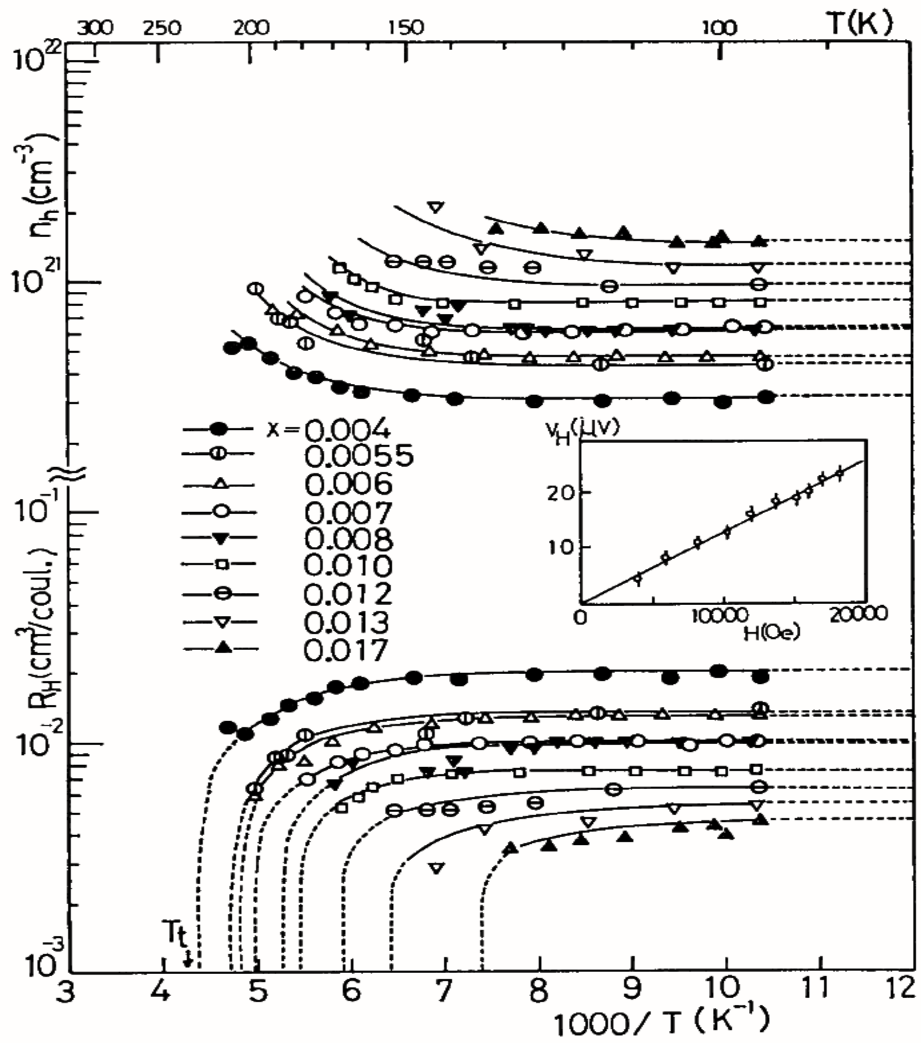


Fig. 5. The Hall coefficient of $Ni_{1-x}S$ (0.004 $\leq x \leq$ 0.017) as a function of 1000/T (the lower part), and the carrier (hole) concentration calculated by $R_H = 1/ne$ (the upper part). The inset illustrates the applied magnetic field dependence of Hall voltage for $Ni_{0.996}S$ at 78 K.

- ❖ Resistivity of ~ 10^{-3} Ω-cm implies
- ❖ If it is an insulator, it has a gap m
- ❖ Carrier concentration drops by a
- ❖ Sizable amount of carriers (~10^{20} phase. **(Metal?!)**
- ❖ But extrapolation to stoichiometr vanishingly small carrier concentrati
- ❖ Carrier changes sign from negati

(iii) Optical Conductivity

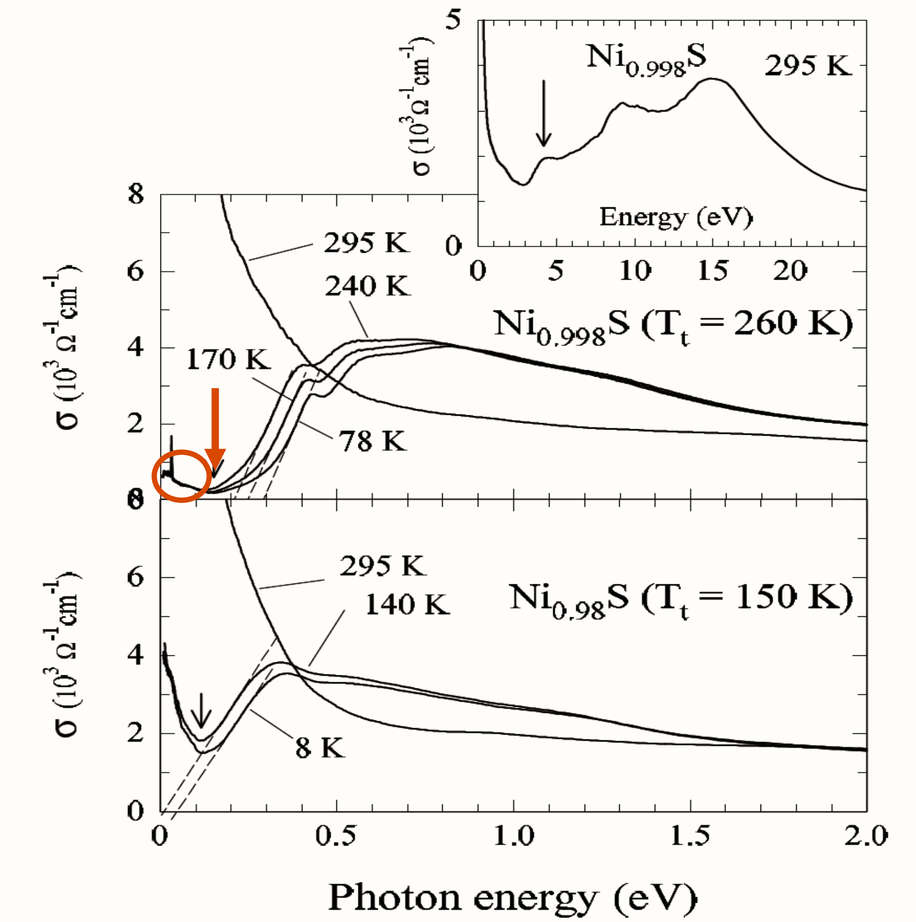


Fig. 3. Optical conductivity spectra (σ) of $Ni_{0.998}S$ and $Ni_{0.98}S$ below 2.0 eV at several temperatures. The arrows indicate the "onset" discussed in the text, and the dashed straight lines are fitted to the linearly rising portion of σ. The inset shows σ of $Ni_{0.998}S$ at 295 K up to 25 eV, and the arrow indicates the peak due to *d*–*d*

- ❖ **Spectral weight below ~0.3 eV is strongly depleted with an "onset" of σ(ω) at ~0.15 eV.**

- ❖ **Below the onset, there exist a small rise in σ(ω).**
- ❖ **This Drude like component indicates that there are sizable amount of free carriers.**

Okamura *et al*, SSC,112,91(1999)

- ➢ **Low temperature phase is a carrier doped semiconductor with an energy gap ~0.2 eV**

- ➢ **System is a semimetal, that has low carrier concentration and a strong reduction in DOS around E_F (a pseudo gap).**

(iv) Photoemission

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Opening of a Correlation-Induced Band Gap in NiS

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(Received 29 July 1994)

We have measured hi which undergoes a nonmetal-metal transition at $T_t \sim 260$ K ıd edge is essentially a step function broadened only by ~ 1! ıcile with one-electron band theory, which predicts a much nfluence of electron correlation on quasiparticle excitations tiferromagnetic insulators.

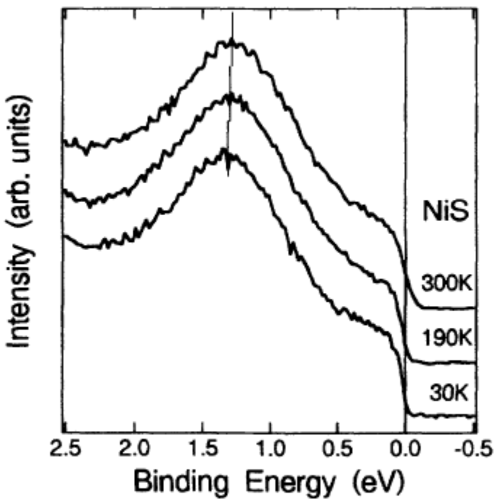

FIG. 1. Photoemission spectra of NiS.

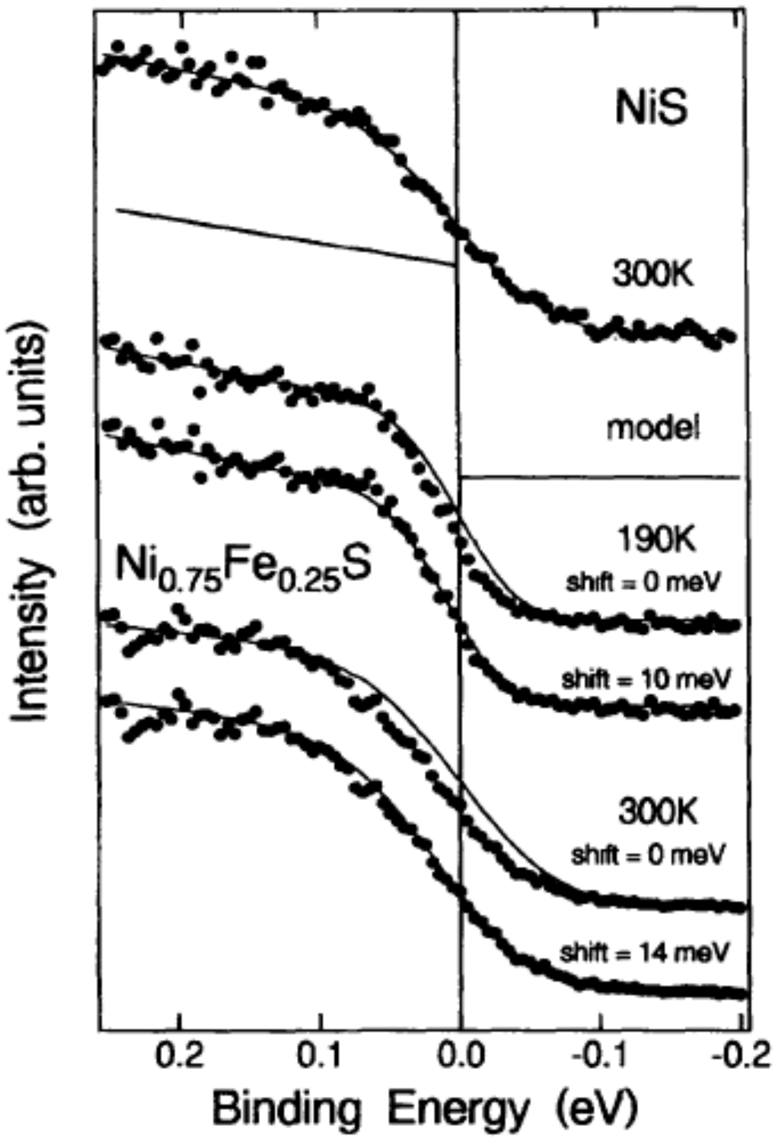

FIG. 3. Comparison of the spectra (dots) with a nearly flat DOS multiplied by a Fermi distribution function (solid curves). For $T < T_t$, the Fermi function has been shifted towards higher binding energies.

Electronic Structure of $NiS_{1-x}Se_x$ across the Phase Transition

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(Received 3 September 1997)

We report very highly resolved photoemission spectra of $NiS_{1-x}Se_x$ across the so-called metal-insulator transition as a function of temperature as well as composition. The present results convincingly demonstrate that the low temperature, antiferromagnetic phase is metallic, with a reduced density of states at E_F. This decrease is due possibly to the opening of gaps along specific directions in the Brillouin zone caused by the antiferromagnetic ordering. [S0031-9007(97)05260-5]

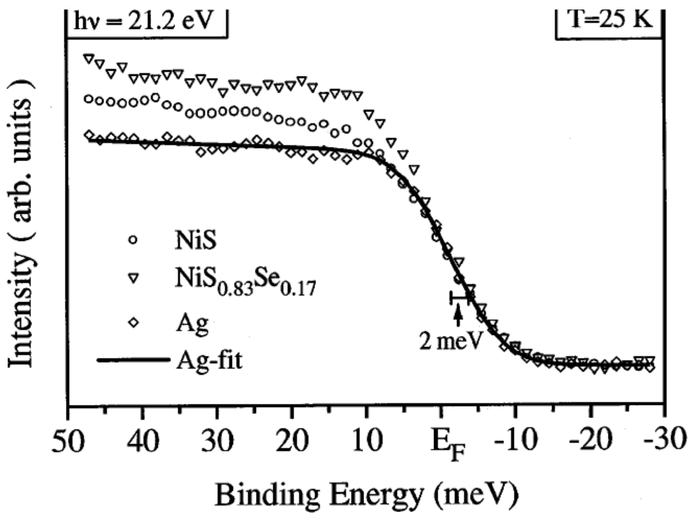


FIG. 1. PE spectra of polycrystalline NiS, $NiS_{0.83}Se_{0.17}$, and Ag in a narrow region around E_F recorded at 25 K. Within experimental accuracy (<1 meV), all spectra show completely overlapping Fermi cutoffs. The solid line represents a fit of the Ag spectrum with an experimental resolution of 9 meV (FWHM).

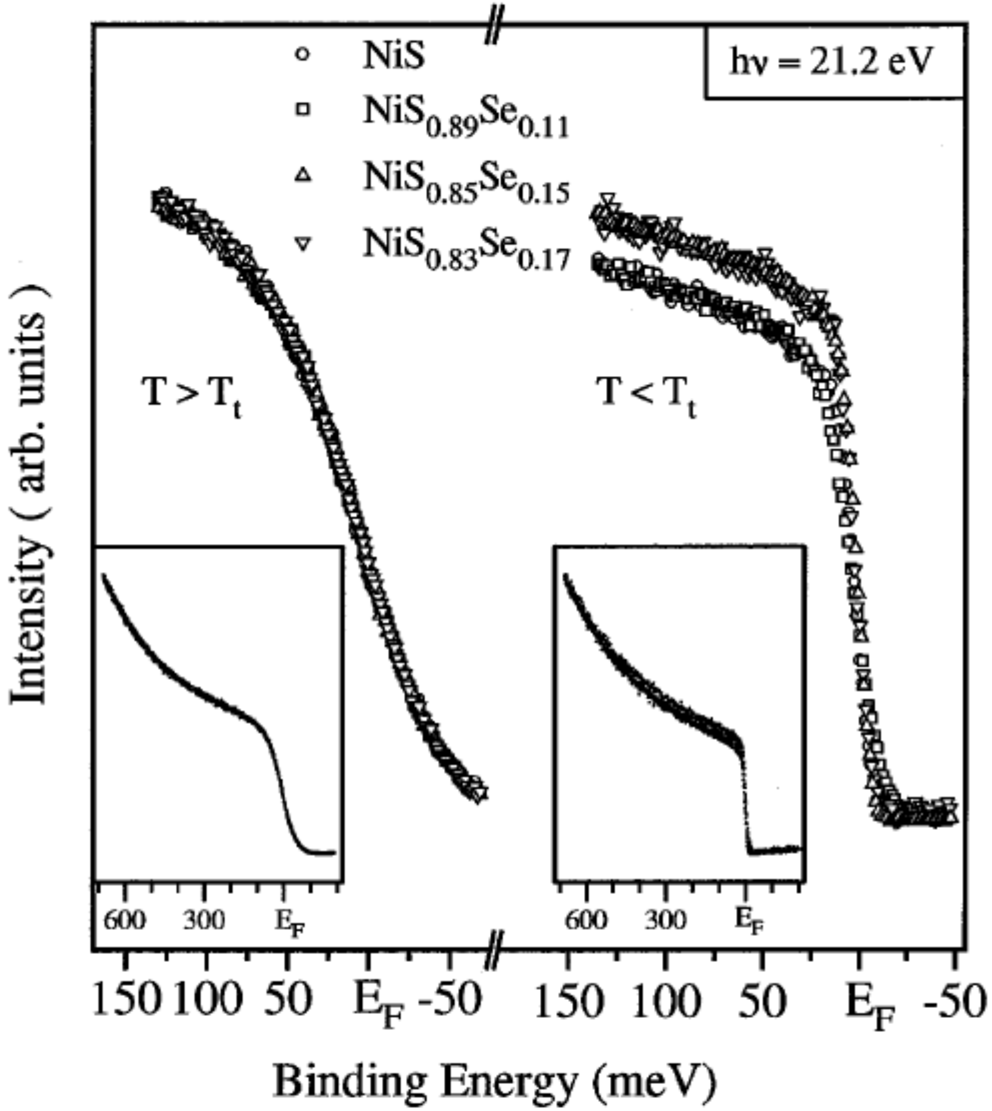
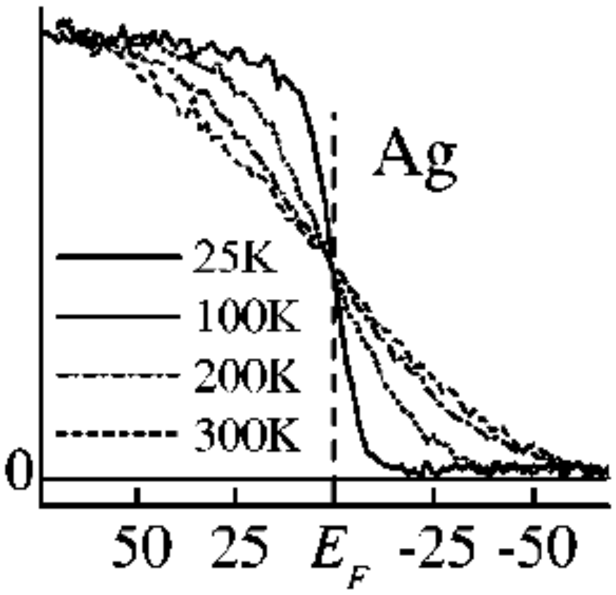
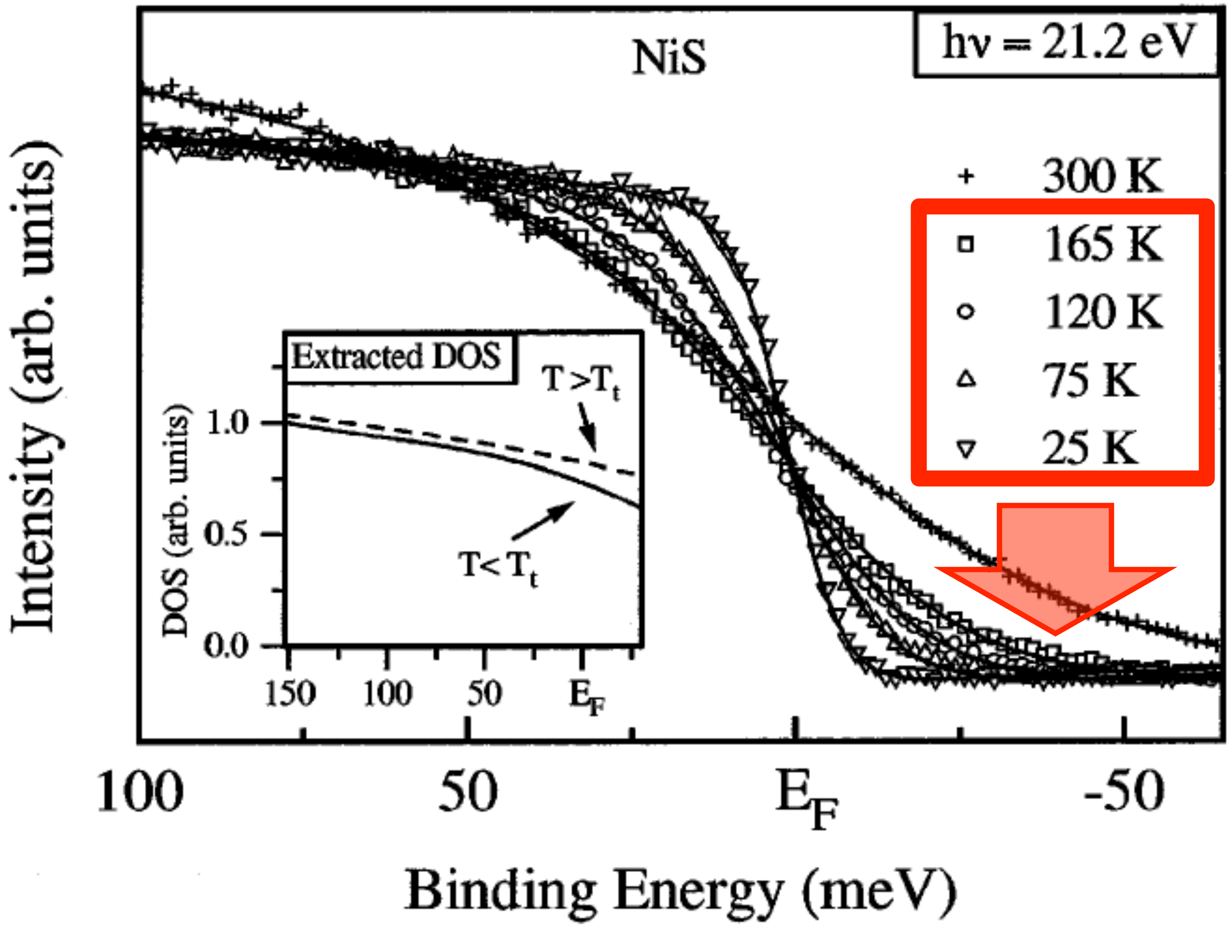


FIG. 2. PE spectra of $NiS_{1-x}Se_x$ with $x = 0.0$, 0.11, 0.15, and 0.17, recorded above (left) and below (right) the transition temperature T_t. For $T > T_t$ all samples show the same spectral weight at E_F, while for $T < T_t$ a substantial decrease is observed for NiS and $NiS_{0.89}Se_{0.11}$. The insets display a wider energy range, demonstrating the proper normalization of the spectra.



Metal

But with a reduced spectral weight



Looks exactly like Ag!

Sizable spectral weight by thermal excitation at least up to ~40 meV above E_F.

FIG. 3. PE spectra of NiS recorded at various temperatures below the phase transition temperature T_t (open symbols), together with a 300 K spectrum. The inset displays the derived DOS for $T > T_t$ and $T < T_t$.

With so much of experimental data available, the system is over-determined!

Theoretical Scenario

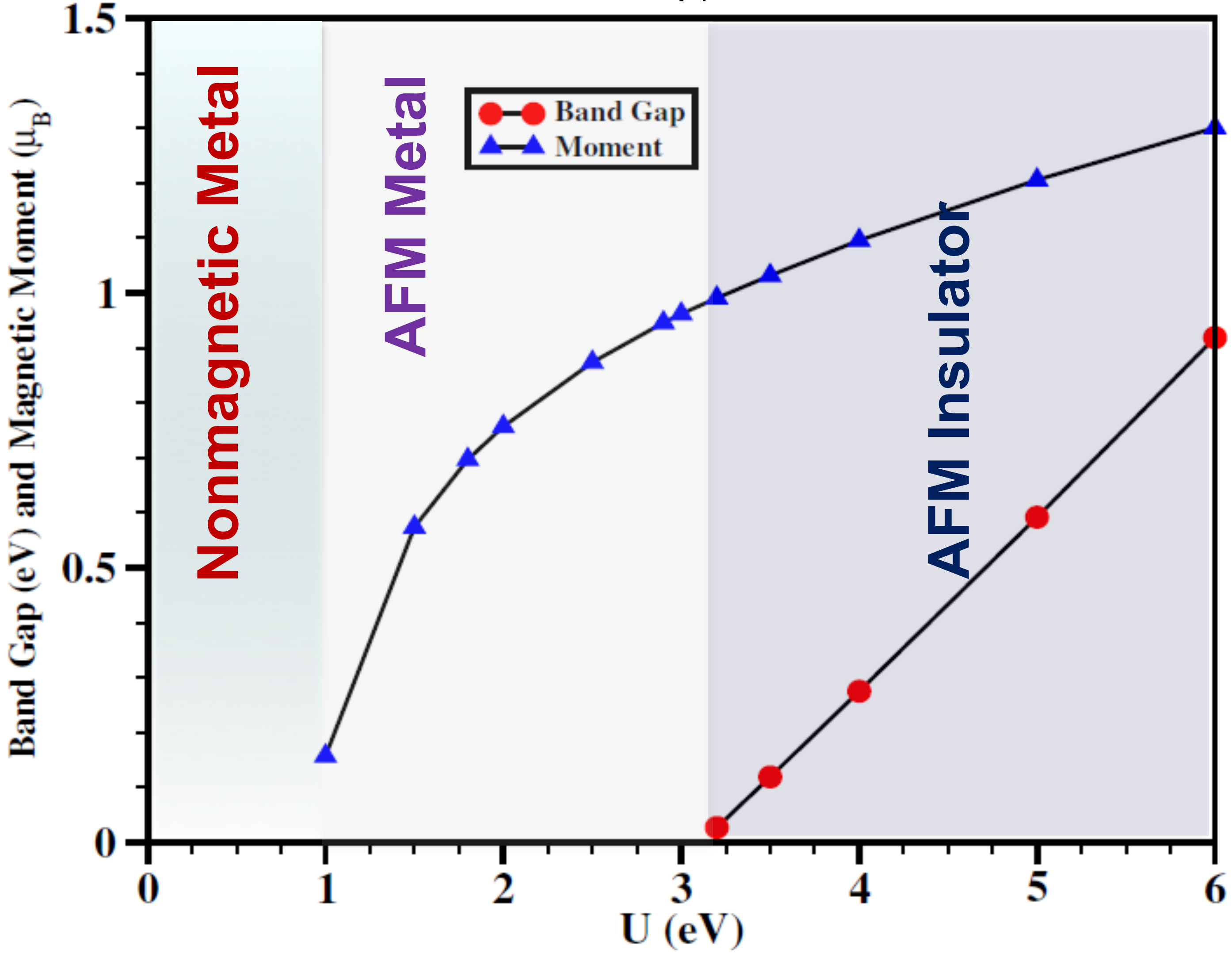
- ❑ **Anisimov *et al*. reported a metallic solution employing LSDA+U calculation by means of the LMTO method.**

Anisimov et al, PRB 44, 943 (1991)

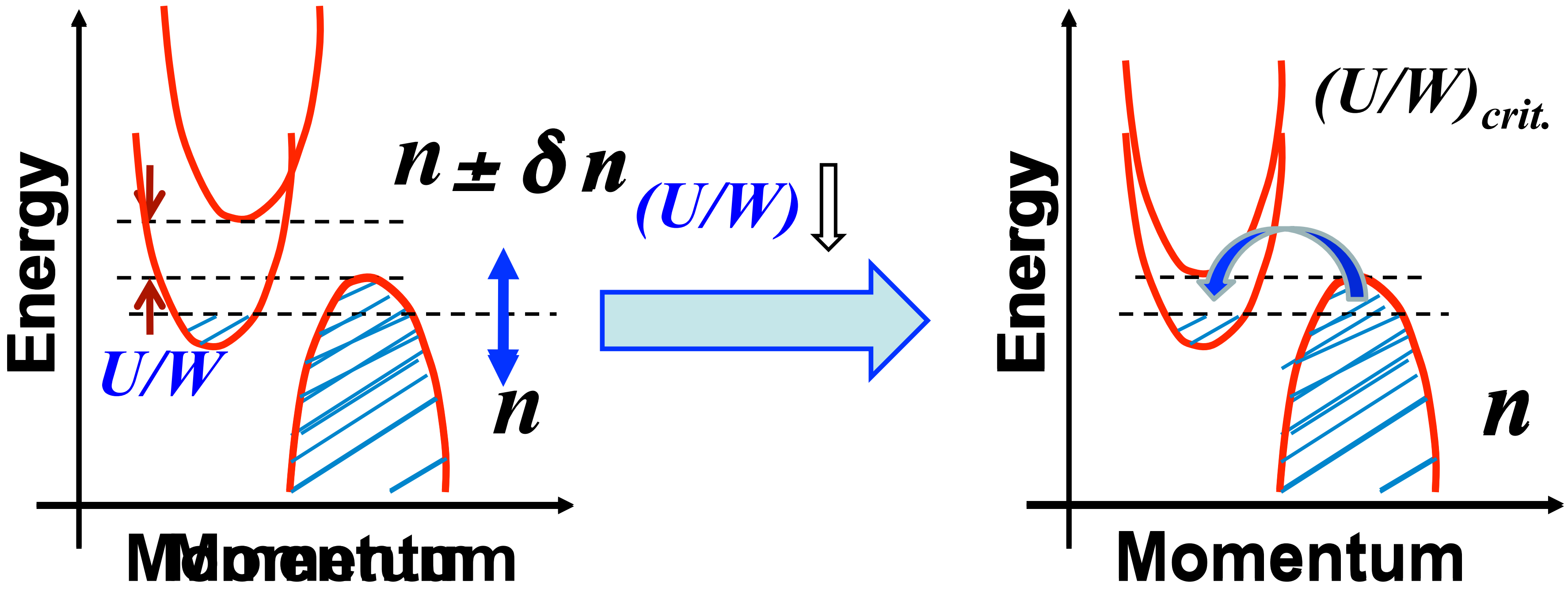
- ❑ **Usuda *et al* reported an antiferromagnetic insulating ground state with an energy gap ~0.1 eV for $U_{Ni\ 3d}$ = 2.85 eV using FPLAPW calculation in the LSDA+U approach.**

Usuda et al, J. Phys Soc. Jap. 69, 744 (1999)

Phase Diagram of NiS



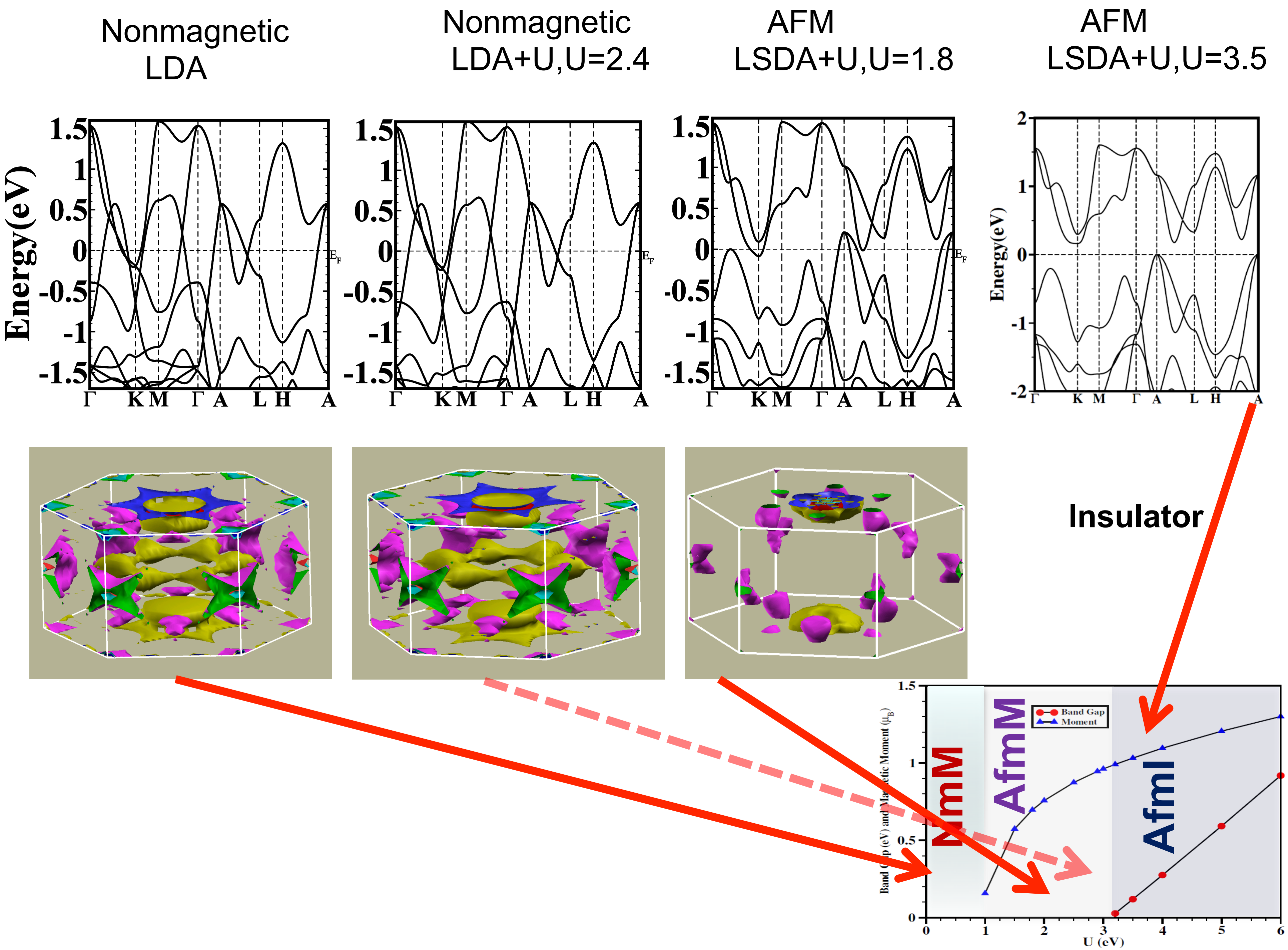
- For U<1 eV, every calculation converged to a non-magnetic solution.
- For U≥1 eV, antiferromagnetic state is always the ground state.
- For 1 eV≤U<3.2 eV, AFM state is metallic. For U≥3.2 eV, AFM state is insulating and band gap changes linearly with increasing the value of U.



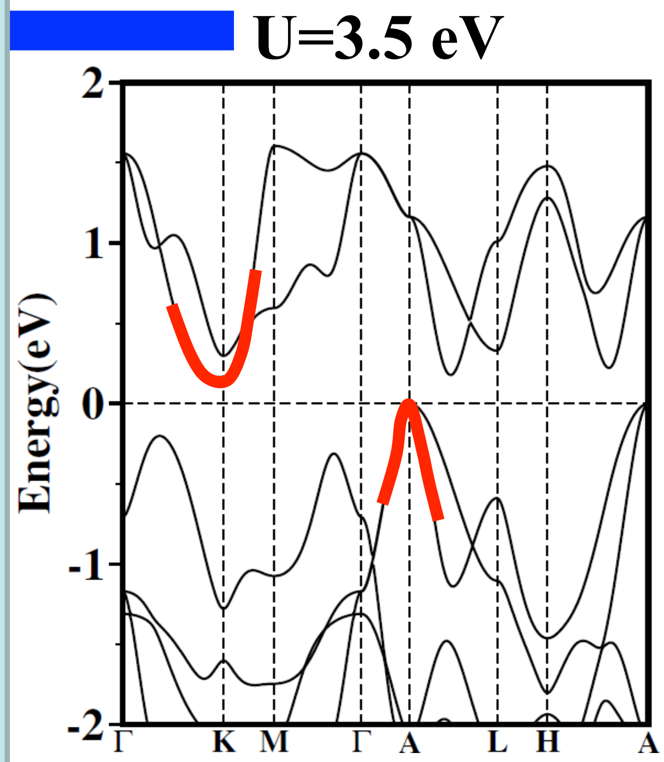
Insulator

Metal

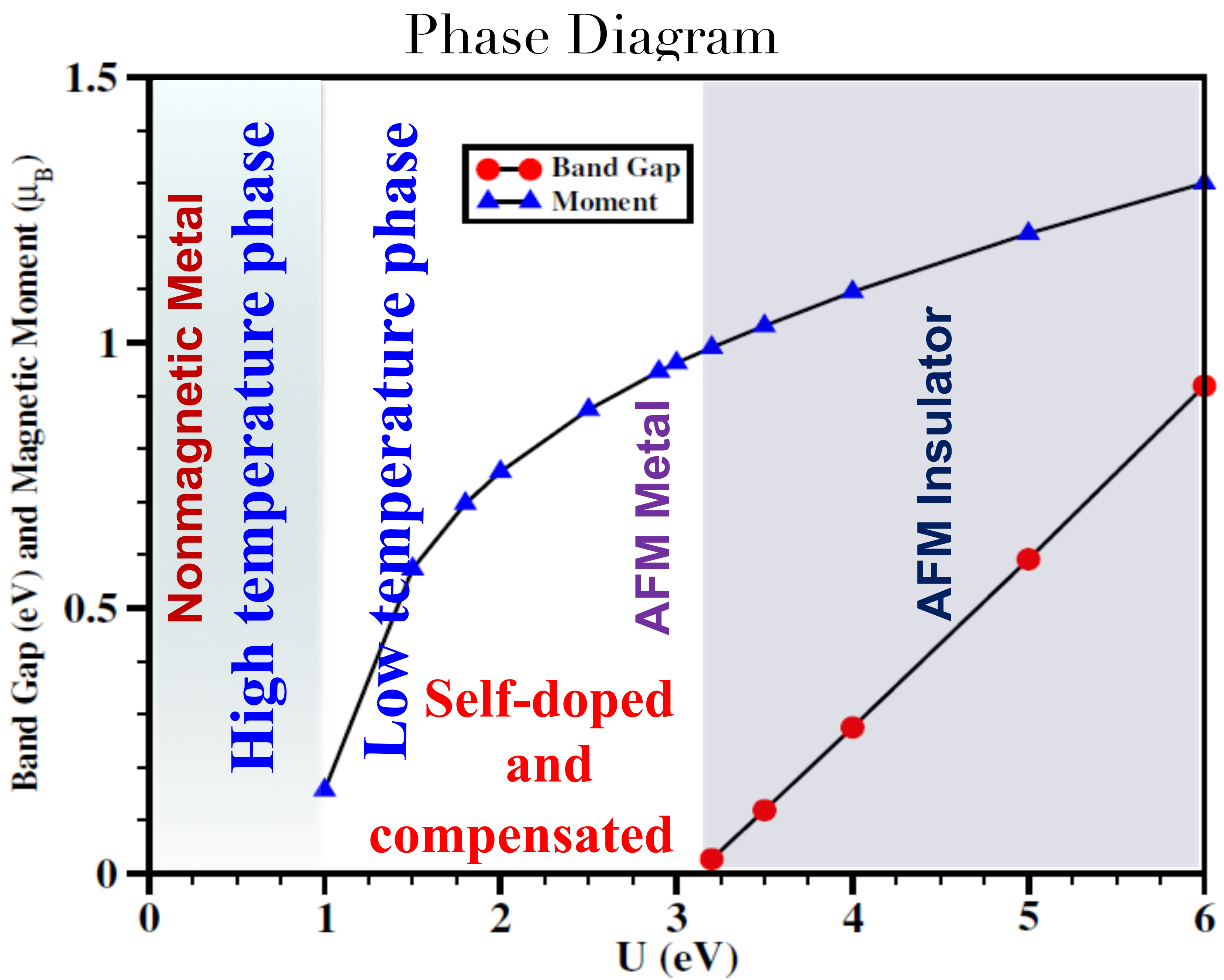
Bad metal behavior in Mott systems



Nonmagnetic
LDA
Nonmagnetic
LDA+U,U=2.4
AFM
LSDA+U,U=1.8
AFM
LSDA+U,U=3.5
Energy(eV)
Γ K M Γ A L H A
Insulator
Band Gap (eV) and Magnetic Moment (μB)
U (eV)
Band Gap
Moment
NmM
AfmM
AfmI

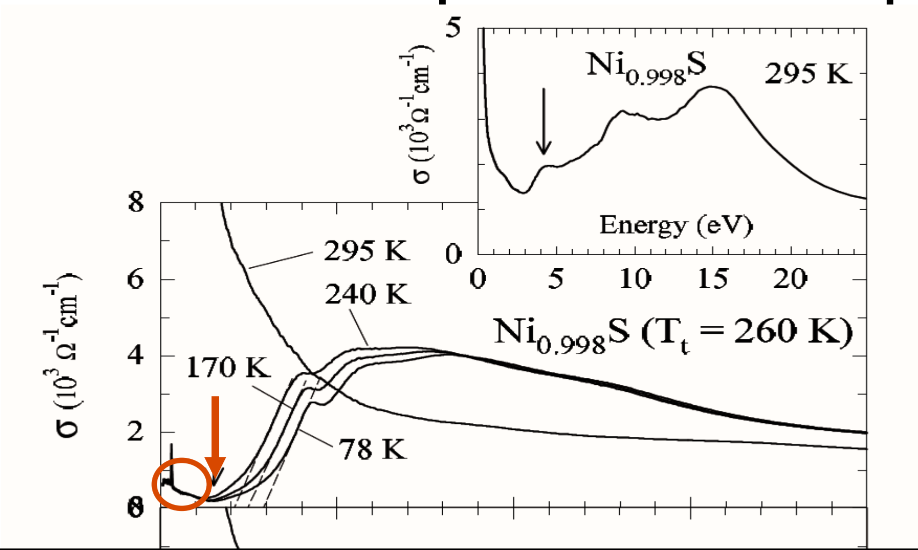


Insulator



Phase Diagram
Band Gap
Moment
Nonmagnetic Metal
High temperature phase
Low temperature phase
AFM Metal
AFM Insulator
Self-doped
and
compensated
Band Gap (eV) and Magnetic Moment (μ_B)
U (eV)
1.5
1
0.5
0
0
1
2
3
4
5
6

Experimental Optical Conductivity



"onset" discussed in the text, and the dashed straight lines are fitted to the linearly rising portion of σ. The inset shows σ of Ni$_{0.998}$S at 295 K up to 25 eV, and the arrow indicates the peak due to d–d

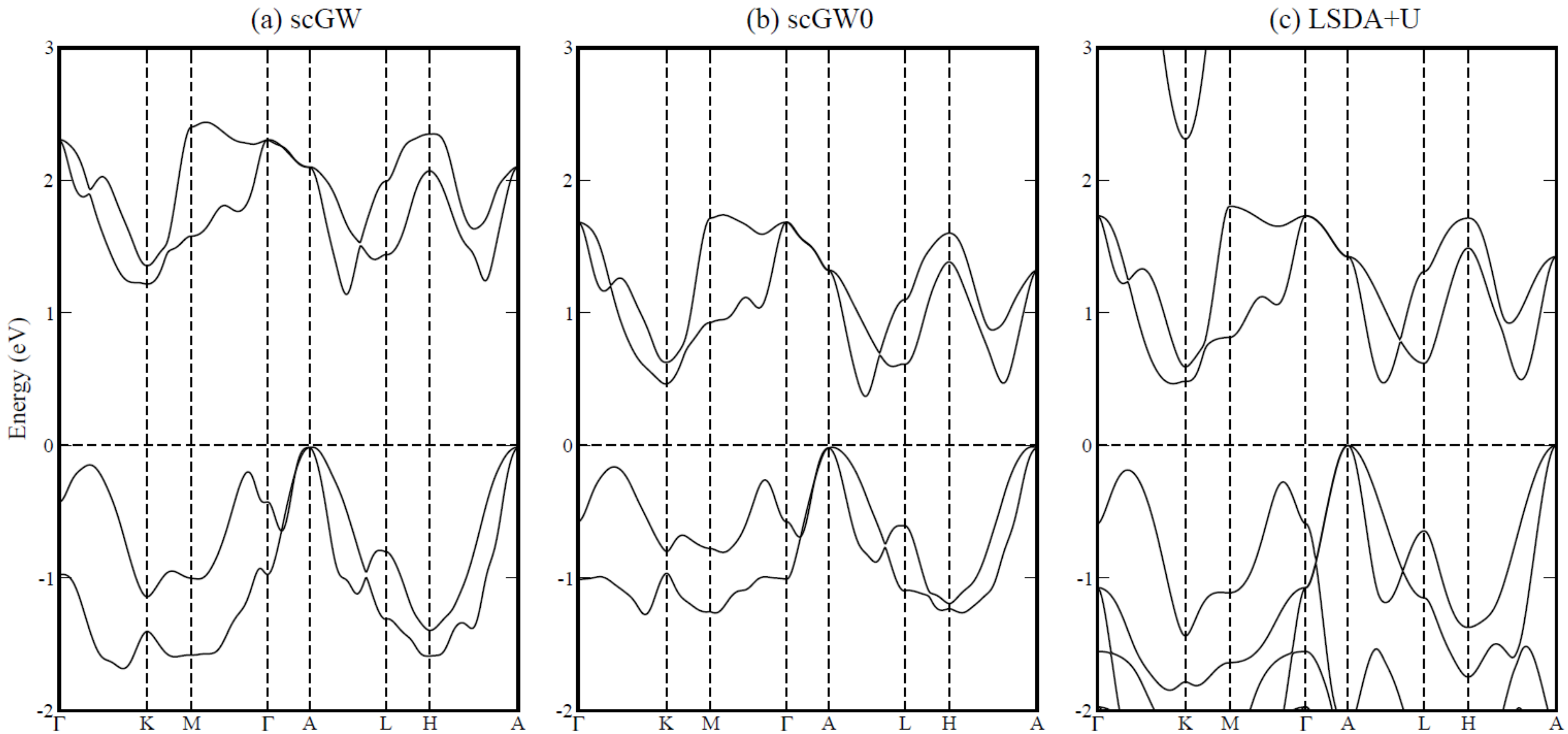
- ❖ **Spectral weight below ~0.3 eV is strongly depleted with an "onset" of σ(ω) at ~0.15 eV.**

- ❖ **Below the onset, there exist a small rise in σ(ω).**
- ❖ **This Drude like component indicates that there are sizable amount of free**

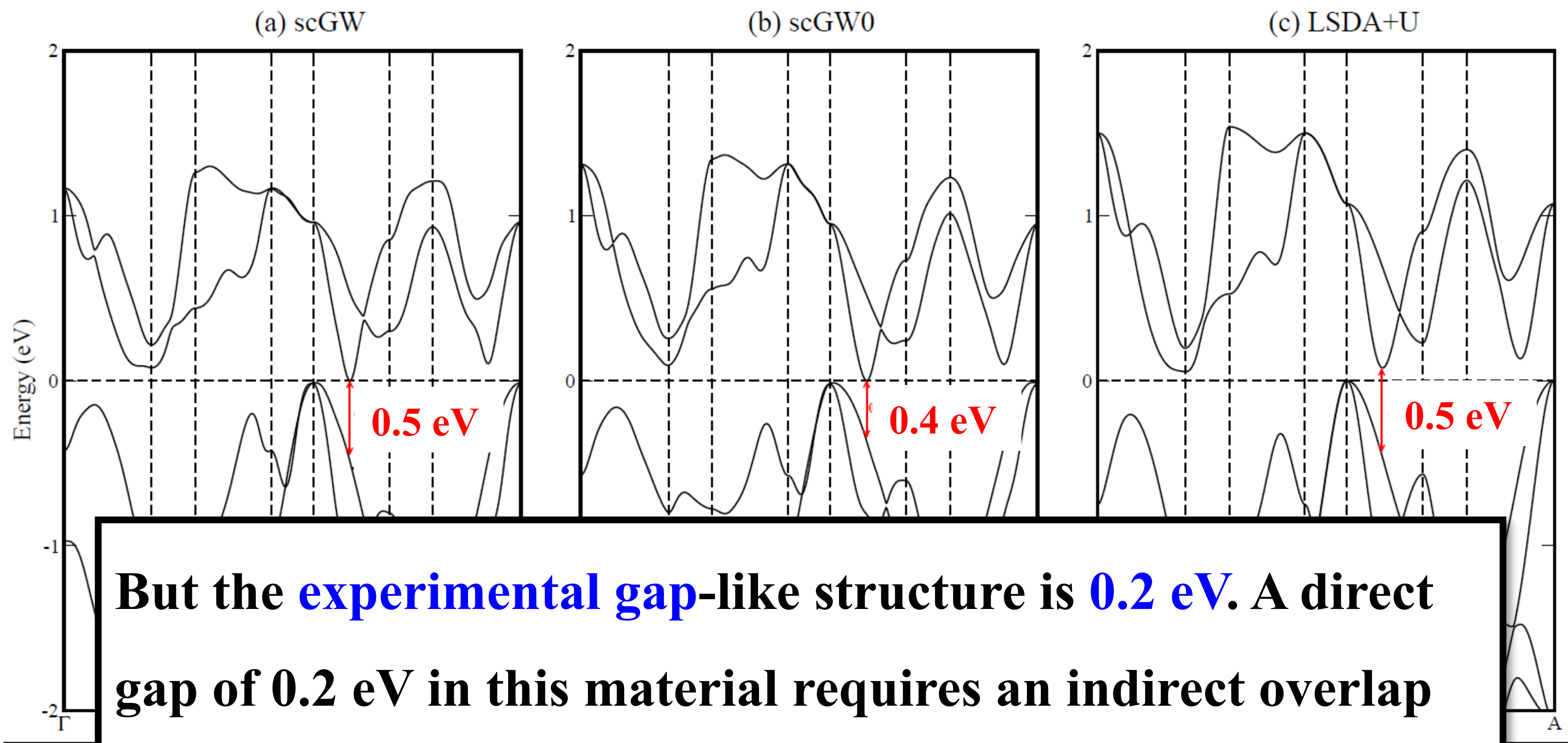
How do we understand the **gap-like feature** in the optical conductivity?

- ➢ **Low temperature phase is a carrier doped semiconductor with an energy gap ~0.2 eV**

- ➢ **System is a semimetal, that has low carrier concentration and a strong reduction in DOS around E_F (a pseudo gap).**

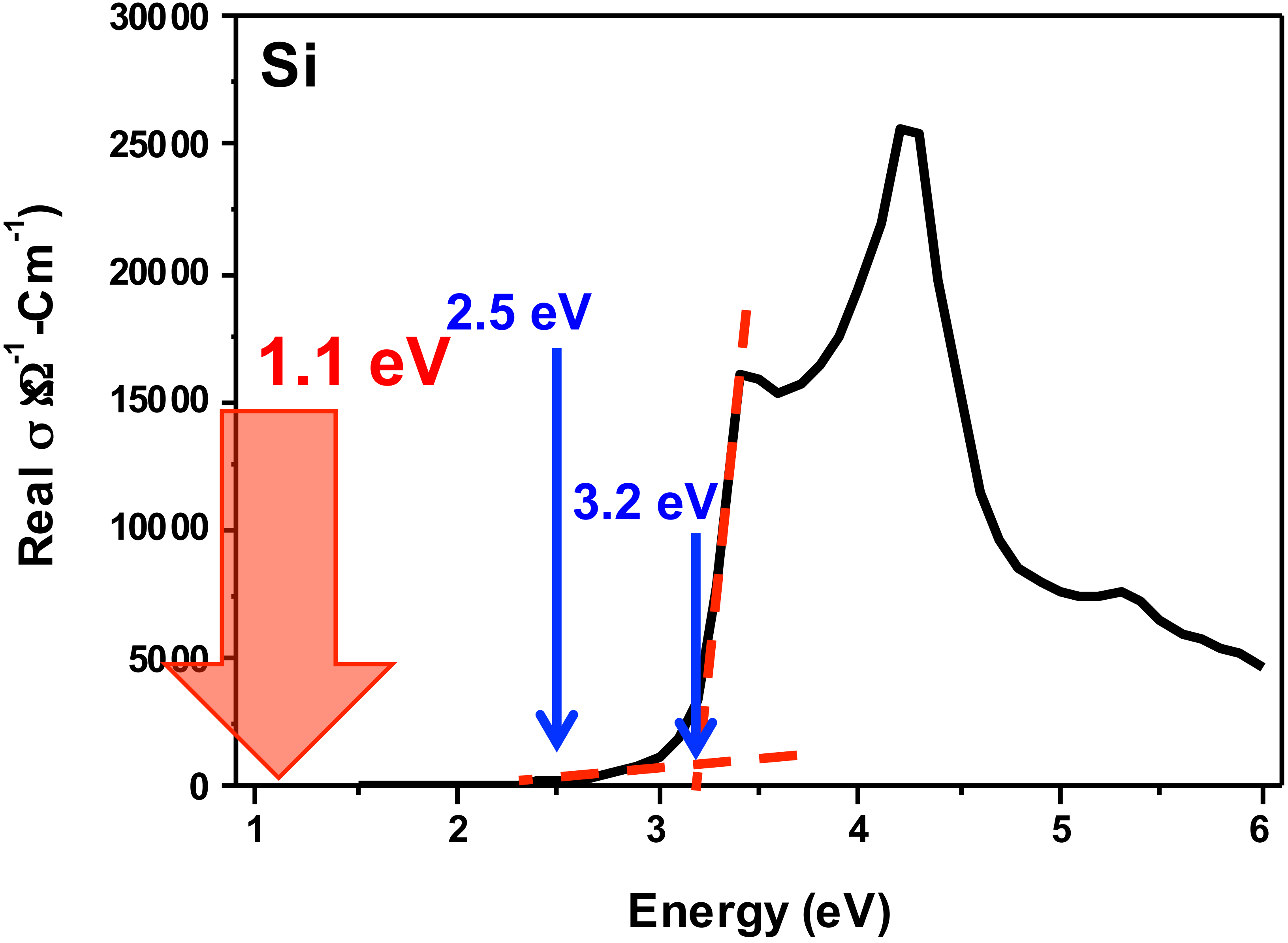


Band dispersion of NiS in the antiferromagnetic insulating regime plotted along various high symmetry directions computed within (a) scGW, (b) scGW0, and (c) LSDA+U (with U = 4.5 eV) methods. The figure shows that the essential qualitative parts of the electronic band dispersions remain identical, irrespective of the calculation method used, indicating NiS to be an indirect gap insulator.

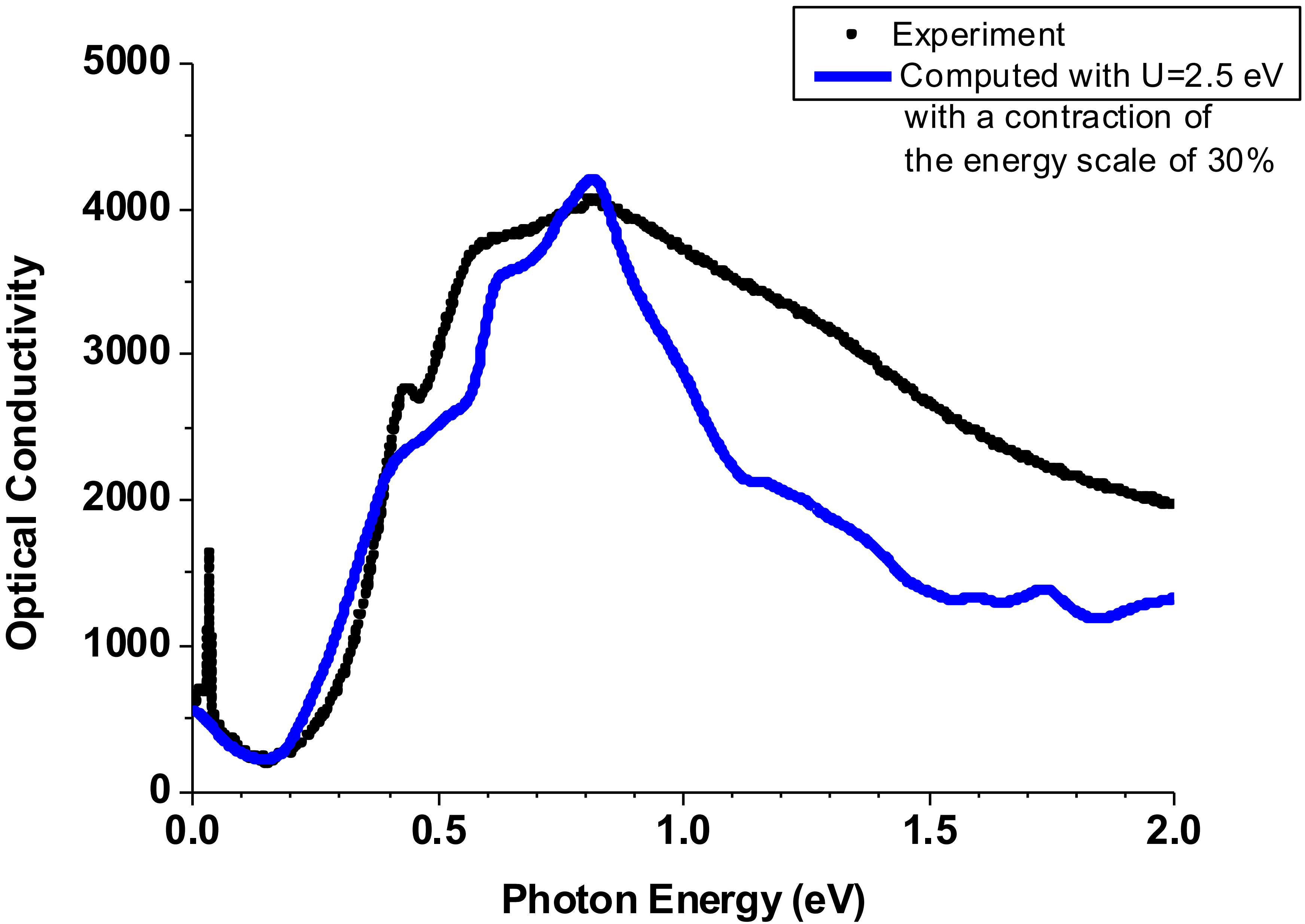


But the experimental gap-like structure is 0.2 eV. A direct gap of 0.2 eV in this material requires an indirect overlap of bands, making the system metallic and yet with an optical gap along with a Drude-like peak at the low energy!

Band dispersion for AFM NiS obtained by (a) scGW and (b) scGW0, where the band gap is made infinitesimally small by vertically shifting the band dispersions of all unoccupied states down, a procedure often termed as "the scissors operator". (c) Band dispersion computed within LSDA+U method with U = 3.15 eV which gives an infinitesimally small band gap. Arrow in each panel indicates the optical gap where in each case it is much larger than the experimental gap of 0.2 eV.

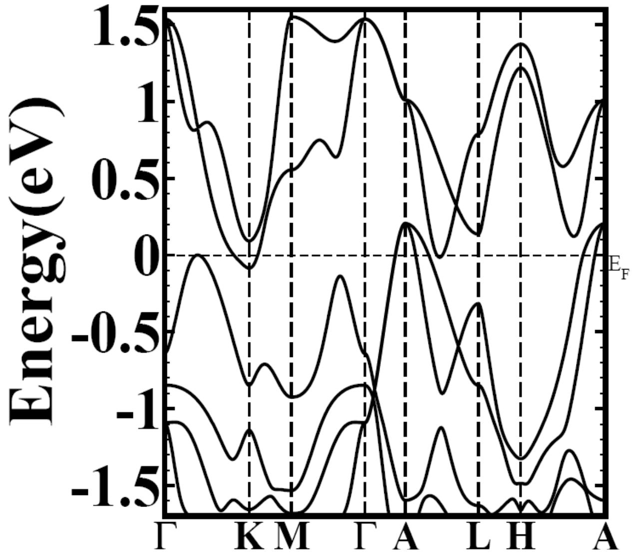


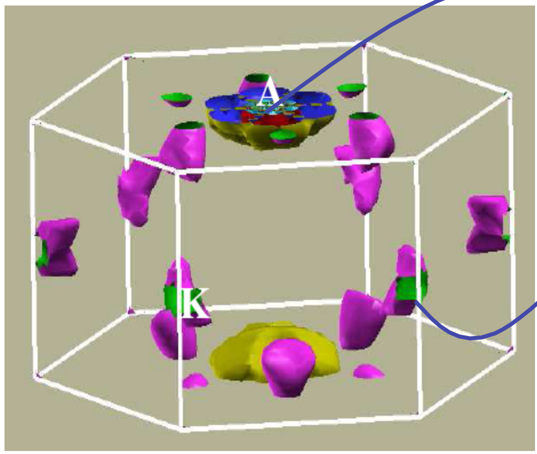
Si
1.1 eV
2.5 eV
3.2 eV
Real σ (Ω⁻¹-Cm⁻¹)
Energy (eV)
0
5000
10000
15000
20000
25000
30000
1
2
3
4
5
6



Experiment
Computed with U=2.5 eV
with a contraction of
the energy scale of 30%
5000
4000
3000
2000
1000
0
Optical Conductivity
0.0
0.5
1.0
1.5
2.0
Photon Energy (eV)

Band Dispersion and Fermi Surface





- **Two hole pockets** at A point and **electron pocket** at K point.
- Carrier Concentration of both the type can be calculated from the volume of this two pockets.

$$R_H = \frac{1}{e}\frac{n_{lh}\mu_{lh}^2 + n_{hh}\mu_{hh}^2 - n_e\mu_e^2}{(n_{lh}\mu_{lh} + n_{hh}\mu_{hh} + n_e\mu_e)^2}$$

$$R_H = \frac{1}{e}\frac{\frac{n_{lh}}{m_{lh}^{*2}} + \frac{n_{hh}}{m_{hh}^{*2}} - \frac{n_e}{m_e^{*2}}}{(\frac{n_{lh}}{m_{lh}^{*}} + \frac{n_{hh}}{m_{hh}^{*}} + \frac{n_e}{m_e^{*}})^2}$$

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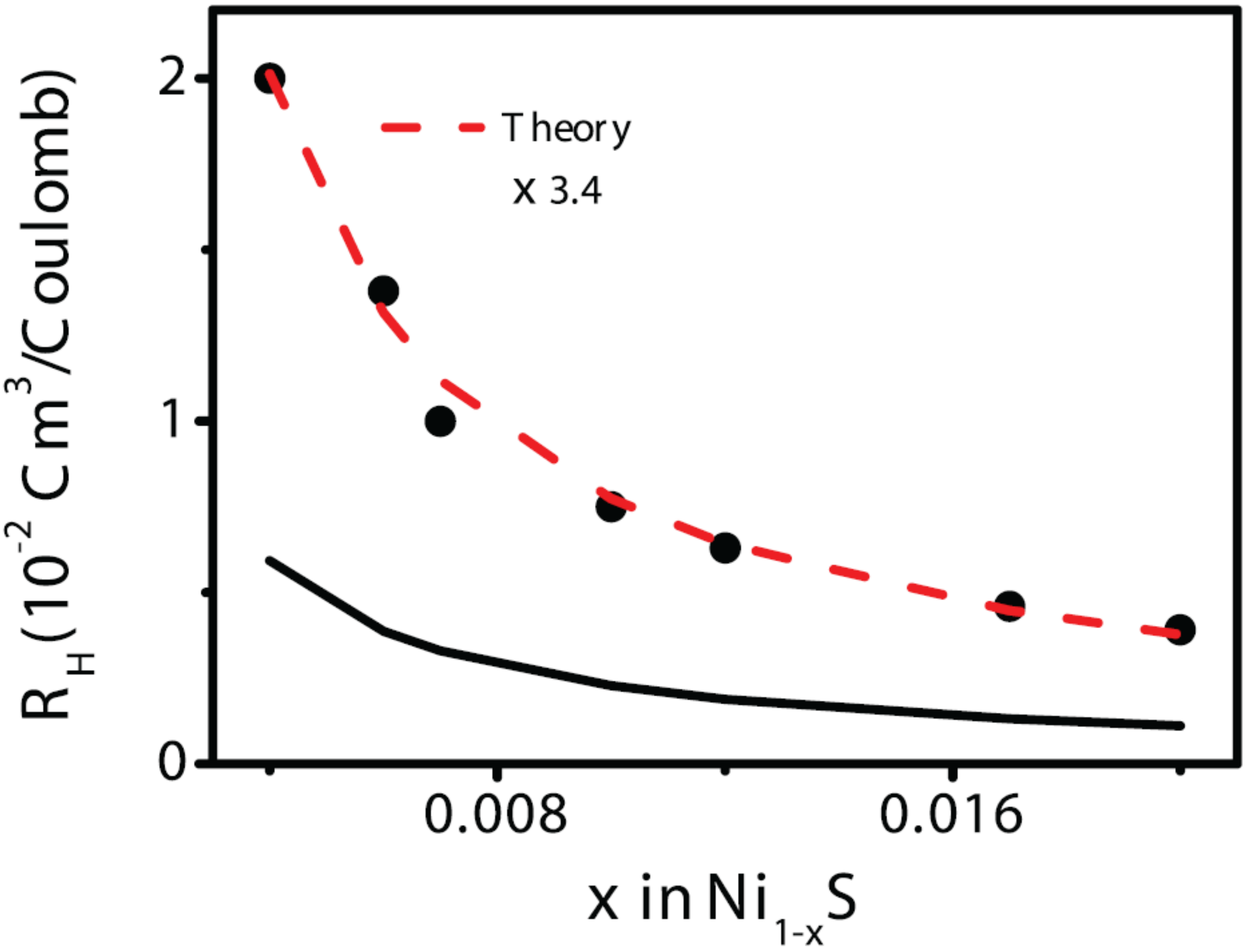

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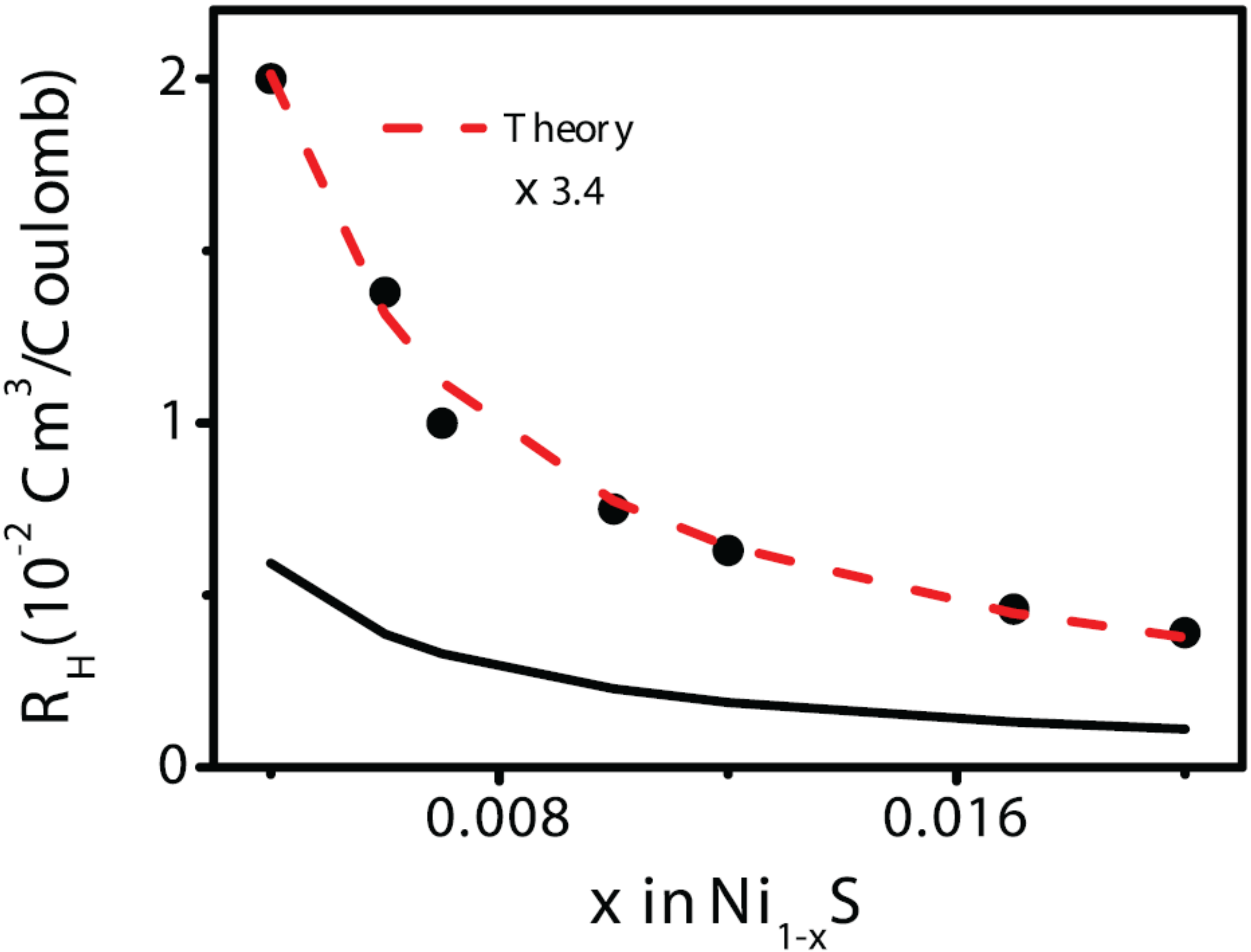
Resistivity

$$\rho = \frac{1}{e(n_{lh}\mu_{lh} + n_{hh}\mu_{hh} + n_e\mu_e)}$$

$$\rho = \frac{1}{eK(\frac{n_{lh}}{m^*_{lh}} + \frac{n_{hh}}{m^*_{hh}} + \frac{n_e}{m^*_e})}$$



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DOS and Photoemission Intensity

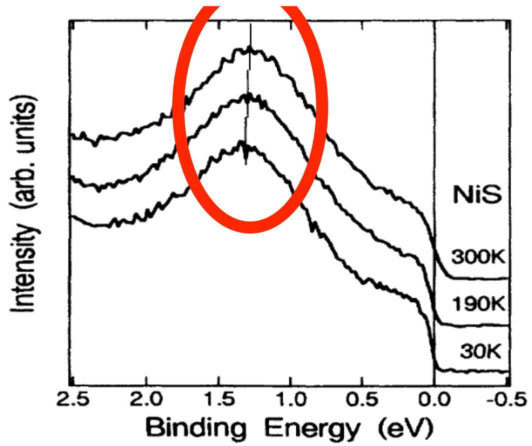

FIG. 1. Photoemission spectra of NiS.

- ❖ Calculated DOS at the Fermi-level in the AFM phase= 1.66×10^{22} states/Cm^3-eV and in the non-magnetic phase is 4.21×10^{22} states/Cm^3-eV.
- ❖ Decrease in DOS at Fermi-level is consistent with experiment.

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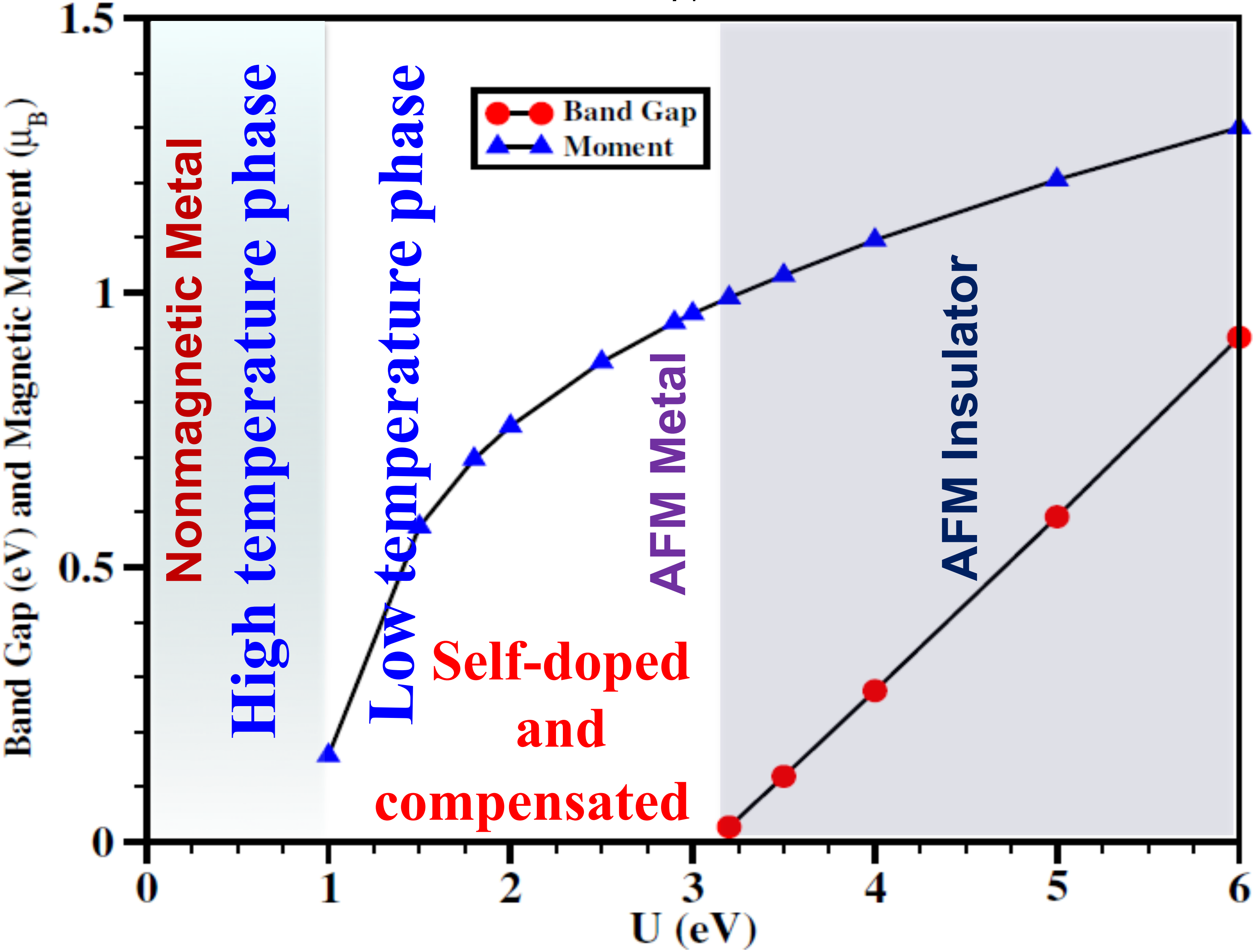
Phase Diagram



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Why should *U* be so different between the NMM and AFM states?

Within the constrained self-consistent, random-phase approximation, we calculate:

- ***U* = 1.8 eV for the high temperature metallic phase.**
- ***U* = 3.7 eV for the low temperature antiferromagnetic phase,**

suggesting a change of about 1.9 eV between the two phases.

Concluding Remarks

The low temperature phase of the hexagonal NiS is a *self-doped,* nearly compensated, relatively low density antiferromagnetic metal.

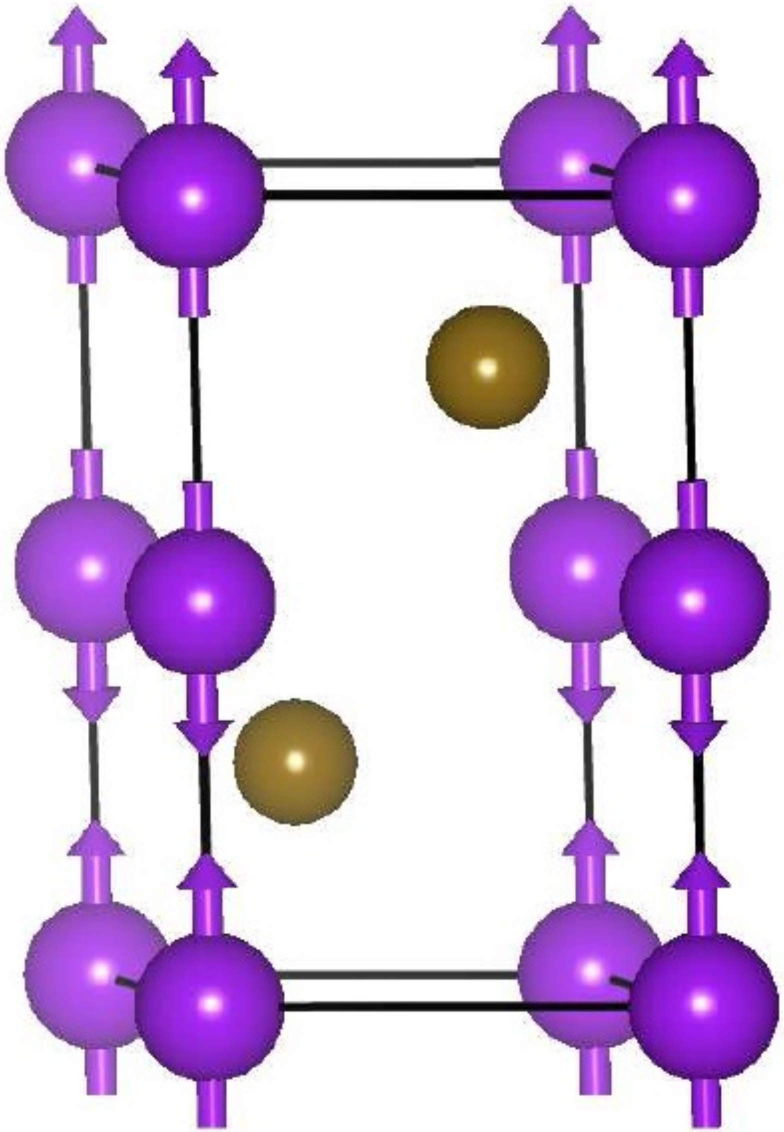
Invitation

#1: To get a First-principle description of the low-temperature phase of NiS: ***U-values, energy agreement (cf. contraction), other quantitative details, such as the change in the spectral weight across the phase transition.***

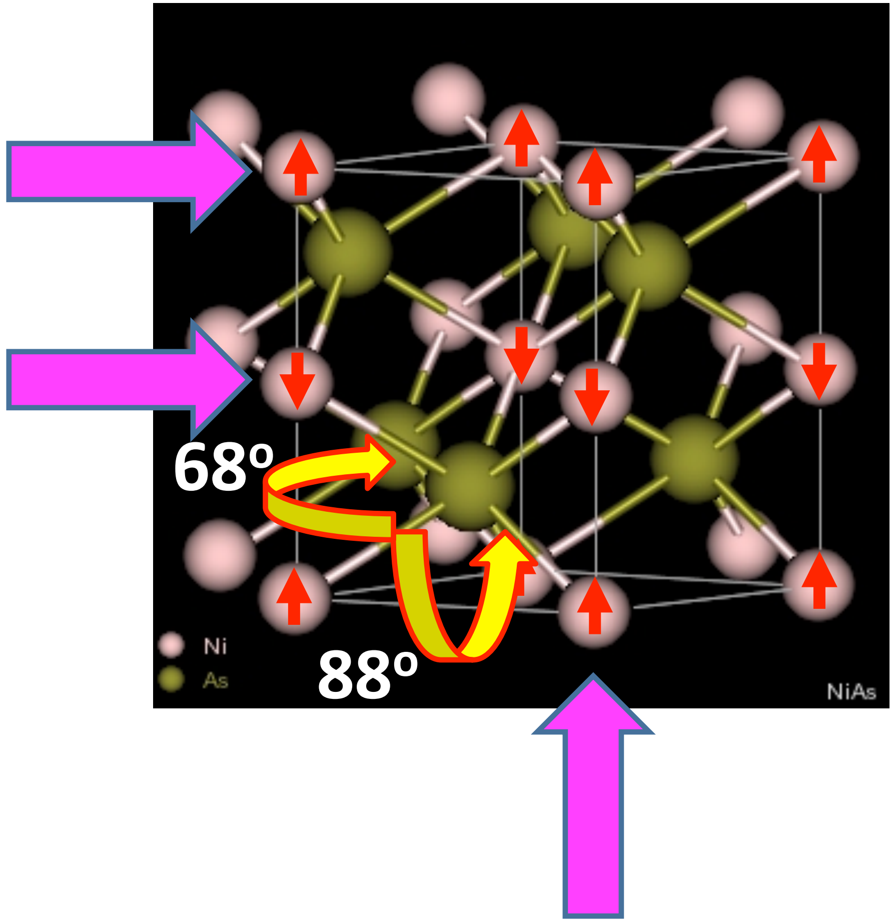
LDA+DMFT by Panda *et al.*
New J. Phys. 16, 093049 (2014).

#2: Explanation of the highly resistive state, T-independence of the resistivity and a proper description of the phase transition.

Magnetism in NiS



NiAs structure
NiS



Thank you for your attention