



# Oxygen vacancy-driven orbital multichannel Kondo effect in Dirac nodal line metals IrO<sub>2</sub> and RuO<sub>2</sub> Juhn-Jong Lin 林志忠

## A Long Journey into Exotic Kondo Physics

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#### SCIENCE ADVANCES | RESEARCH ARTICLE

#### PHYSICAL SCIENCES

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# Probing nanocrystalline grain dynamics in nanodevices

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We demonstrate theoretical conception and experimental method to quantitatively characterize nanocrystallite motion in RuO<sub>2</sub> nanowires.





#### polycrystalline nanowire



## Keywords:

## Kondo physics

Magnetic spin-half Kondo effect Nonmagnetic orbital Kondo effect One-channel Kondo effect Two-channel Kondo effect



A defect having two equivalent (nearby) sites in a solid An object switching in a double-well potential, modeled as a two-level system



**Dynamic defects** 

**Two-level** systems

**Defect electrons** 

Fast two-level systems

Dynamic scattering centers

## Noise due to atomic and granular dynamic defects

The motion of a large number of slow dynamic defects causes low-frequency (1/f) noise.



The motion of a single nanocrystallite leads to random telegraph noise.





"Strong electron correlations may give rise to an unconventional metallic state accompanying non-magnetic Kondo scattering. Here, the authors report signatures of orbital one- and two-channel Kondo physics in Dirac nodal line metals RuO<sub>2</sub> and IrO<sub>2</sub> nanowires."

Experimental realization of non-Fermi liquid behavior at low temperatures!

# Spin-half magnetic Kondo effect

## A localized S = ½ magnetic impurity causes the standard Kondo effect

Experimental discovery in 1930s at Kamerlingh Onnes' Lab. (Leiden) Theoretical explanation in 1960s

W.J. de Haas and G.J. van den Berg (1936)





Comparison of experimental and theoretical  $\rho(T)$  curves for dilute <u>Au</u>Fe alloys [J. Kondo, Prog. Theor. Phys. **32**, 37 (1964)]

## Kondo resistivity: universal temperature dependence



Normalized Kondo resistivity vs. reduced temperature  $T/T_{K}$ (Taken from "Long Range Order in Solids", by R. M. White and T. H. Geballe, Fig. VII.14)



Numerical renormalization group (NRG) calculations: one-channel Kondo (1CK) scaling form

T. A. Costi, A. C. Hewson & V. Zlatic JPCM **6**, 2519 (1994)

## Scattering off a localized spin-half magnetic impurity



- A **nonmagnetic** impurity (defect) in a metal  $\Rightarrow$  Elastic electron scattering
- $\Rightarrow$  A constant, "residual resistivity" at low T



A localized **magnetic** impurity  $(S = \frac{1}{2})$  in a metal  $\Rightarrow$  Spin spin sounling (s d exchange interaction)

- $\Rightarrow$  Spin-spin coupling (s-d exchange interaction)
- $\Rightarrow$  log(T) resistivity increase below a characteristic energy scale T<sub>K</sub>
- $\Rightarrow$  Fermi-liquid physics as T << T<sub>K</sub>





One conduction-electron band (a Fermi sea) couples with the localized spin- $\frac{1}{2}$  magnetic moment, forming a spin-singlet ground state as T  $\rightarrow$  0 K.

## A quantum impurity with internal degree of freedom

Progress of Theoretical Physics, Vol. 32, No. 1, July 1964

#### Resistance Minimum in Dilute Magnetic Alloys

Physica 84B (1976) 40-49 © North-Holland Publishing Company

#### Cf. Localized magnetic moments

LOCALIZED ATOMIC STATES IN METALS

Physica 84B (1976) 207-212 © North-Holland Publishing Company "We investigate a case where the interaction is of the Coulomb type, which may vary depending on the states of the localized system. The simplest of such a system may be an impurity atom, which can jump between two equivalent sites."

 $\Psi = \psi(\vec{r}) \cdot \vec{s}_c \implies \psi(\vec{r}_L), \ \psi(\vec{r}_R)$ 

#### LOCALIZED ATOMIC STATES IN METALS

#### **II. RESISTIVITY AND FREE ENERGY**

J. KONDO

Electrotechnical Laboratory, Tanashi, Tokyo and Department of Applied Physics, Faculty of Engineering, University of Tokyo, Japan

Received 31 May 1976

## A quantum impurity with internal degree of freedom

"The problem is similar to the s-d problem in that the conduction electrons interact with an impurity system having an internal degree of freedom. In the present case, the relevant interaction is the orbital-orbital interaction, since we are considering the Coulombtype interaction."

"Impurity-spin flipping" vs. "Impurity-site switching"

Two equivalent sites Double-well potential  $\Rightarrow$  "Two-level system" model

 $\Rightarrow$  Non-magnetic orbital Kondo effect !

J. Kondo (1976)





## Spin multi-channel Kondo effect

J. Physique 41 (1980) 193-211

MARS 1980, PAGE 193

Classification Physics Abstracts 75.20H

#### Kondo effect in real metals

Ph. Nozières

Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France

and A. Blandin

Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France

(Reçu le 21 septembre 1979, accepté le 30 octobre 1979)

## The multichannel Kondo model:

**A few** conduction-electron bands interact with a localized quantum impurity which has internal degree of freedom.

"Over-screening" shall result in a non-Fermi-liquid ground state.

One-channel Kondo effect
⇒ Fermi-liquid ground state
Multi- (two-) channel Kondo effect
⇒ a non-Fermi liquid ground state
⇒ Strange metal physics

## **Orbital multi-channel Kondo effect**

Exot	ic Kondo effects in metals: magnetic ions in a crystalline electric field and tunnelling centres	344 pages	
	D. L. Cox		
Department of Physics, The Ohio State University, Columbus, Ohio 43210, USA and Department of Physics, University of California, Davis, California 95616, USA			
	and A. ZAWADOWSKI		
Institute of Physics and Research Group of Hungarian Academy of Sciences,			
Techn	PHYSICAL REVIEW BVOLUME 28, NUMBER 3	1 AUGUST 1983	
Theory of the interaction between electrons and the two-level system in amorphous metals. I. Noncommutative model Hamiltonian and scaling of first order			
	K. Vladar Central Research Institute for Physics, Post Office Box 49, H-1525 Budapest, Hungary	I. 18 pag	ges
	A. Zawadowski* Department of Physics, University of California, Los Angeles, California 90024 (Received 10 June 1982)	II. 14 pa III. 17 pa	ges ages

$$H = \sum_{i,k,\sigma} \varepsilon_k \psi_{i,k,\sigma}^{\dagger} \psi_{i,k,\sigma} + J_K \sum_{i=1}^{M=2} \vec{S} \cdot \vec{s}_c^{\ i}$$

- Two-channel Kondo effect
- non-Fermi-liquid ground state

M channels (M Fermi seas)

# Vacancies in ZrAs<sub>1.58</sub>Se<sub>0.39</sub> & two-level systems

Defect potential gives rise to several minima separated by a potential barrier: **two-level systems** 

$$\begin{vmatrix} \uparrow \rangle \\ |\downarrow \rangle$$
 if atom is in  $\begin{cases} left \\ right \end{cases}$  position

## pseudospin algebra



coupling to conduction electrons induces 'assisted' tunneling effective "spin-spin" interaction is very anisotropic

conduction electron spin acts as a bystander

- gives rise to 2 degenerate channels due to time-reversal symmetry
- $\rightarrow$  system should flow to the non-magnetic two-channel Kondo fixed point
- → **insensitivity to applied magnetic fields** (Vladar, Zawadowski, Zarand, von Delft ...)

(courtesy of S. Kirchner)

## Two-level systems: the no-go theorem



\* Stefan Kirchner \*

(courtesy of S. Kirchner)

Nanotechnology has rekindled interest in the Kondo effect, one of the most widely studied phenomena in condensed-matter physics

# **Revival of the Kondo effect**

Leo Kouwenhoven and Leonid Glazman

temperature



The theory that describes the scattering of electrons from a localized magnetic impurity was initiated by the work of Jun Kondo in 1964



A semiconductor quantum dot (~ 100 nm) containing an **odd** number of electrons can act as a localized spin- ½ magnetic impurity, giving rise to Kondo physics

 $\Rightarrow$  Kondo "conductance" G(T)



Drain

A quantum dot (S=1/2) coupled to source-drain electrodes

Goldhaber-Gordon et al., Nature 391, 156 (1998)



temperature

# **Motivation**



The theory that describes the scattering of electrons from a localized magnetic impurity was initiated by the work of Jun Kondo in 1964

two-channel

Nanotechnology has rekindled interest in the Kondo effect, one of the most widely studied phenomena in condensed-matter physics

# **Revival of the Kondo effect**

Leo Kouwenhoven and Leonid Glazman

Phys. World 14, 33 (2001)

## A suggested route to 2CK effect

Vol 446 8 March 2007 doi:10.1038/nature05556

# **Observation of the two-channel Kondo effect**

R. M.  $Potok^{1,3}$ ; I. G.  $Rau^2$ , Hadas Shtrikman<sup>4</sup>, Yuval  $Oreg^4$  & D. Goldhaber-Gordon<sup>1</sup>



**Problems and difficulties:** 

- 1) Fine-tuning is required.
- 2) Implications for real solids and topological quantum materials is unclear.
- 3)  $T_{K}$  value is very small.

$$G(V,T) = \frac{dI(V,T)}{dV}$$

 $\sqrt{T}$  temperature behavior A non-Fermi-liquid signature

nature

LETTERS



## Orbital two-channel Kondo effect in real materials

## **Experimental signature:**

A  $\sqrt{T}$  resistivity increase at low temperatures (in the residual-resistivity regime). The resistivity increase is independent of an applied magnetic field.

$$\Delta \rho_{2CK}(T,B) \propto -n_d \sqrt{T}$$

 $n_d$ : dynamic defect density

## Altshuler & Aronov: An ubiquitous effect in real conductors !

Electron-electron interaction (EEI) effect causes a  $\sqrt{T}$  resistivity increase at low temperatures in 3D weakly disordered metals.

$$\frac{\Delta\rho(T)}{\rho_0} = -\frac{0.915e^2}{4\pi^2\hbar} \left(\frac{4}{3} - \frac{3}{2}F\right) \rho_0 \sqrt{\frac{k_B T}{\hbar D}}$$

*D*: electron diffusion constant  $0 \le F \le 1$ : a screening factor

The presence of impurities cause multiple elastic scattering, leading to quantum interference of electronic waves, which in turn results in enhanced e-e interaction.  $\Rightarrow$  The density of states at  $E_F$  is suppressed.

## IrO<sub>2</sub> and RuO<sub>2</sub> crystalizes in the rutile structure

R(T)/R(300 K)



Ir: [Xe]4*f*<sup>14</sup>5*d*<sup>7</sup>6*s*<sup>2</sup> Ir<sup>+4</sup>: [Xe]4*f*<sup>14</sup>5*d*<sup>5</sup>

5*d* orbitals are half-filled in IrO<sub>2</sub>



T(K)

J. J. Lin et al., JPCM 16, 8035 (2004)

## Recent discovery: Dirac nodal line metals IrO<sub>2</sub> and RuO<sub>2</sub>



# nanowire diameter $\approx 50 - 190 \text{ nm}$



Nanowires were grown by Y.S. Huang's group (NTUST), and F.R. Chen & J.J. Kai's group (NTHU).

- IrO<sub>2</sub> nanowires were grown via MOCVD.
   RuO<sub>2</sub> nanowires were grown via thermal evaporation.
- Four-probe R(T) measurements down to 50 mK, in applied magnetic field up to 9 T.
- Nanowires were measured as-grown, after annealing in vacuum, and after oxygenation.
- Thermal annealing in vacuum generates oxygen vacancies which generate dynamic scattering defects, causing orbital Kondo effect.
- The orbital Kondo effect is suppressed in (fully) oxygenated nanowires.

## Resistivity vs. temperature for IrO<sub>2</sub> and RuO<sub>2</sub> nanowires



The overall resistivity curve  $\rho(T)$  reveals Boltzmann-transport behavior.

The low-T resistivity increase can be repeatedly introduced (suppressed) by thermal annealing in vacuum (oxygen).

# $\sqrt{T}$ resistivity increase in paramagnetic IrO<sub>2</sub> nanowires



• A  $\sqrt{T}$  resistivity increase is found after annealing in vacuum.

• The  $\sqrt{T}$  resistivity increase shows insensitivity to magnetic field.

• After aging in air, the  $\sqrt{T}$  behavior persists, but showing a smaller resistivity increase.

 Oxygenation reduces dynamic scattering defects, producing a smaller orbital Kondo effect.

• A deviation from the  $\sqrt{T}$  behavior occurs around 0.5 K !

## Ruling out 3D electron-electron interaction effect

• A deviation from the  $\sqrt{T}$  dependence at ~0.5 K is incompatible with the 3D EEI effect.

• The observed resistivity increase (~0.5%) is more than one order of magnitude as would be predicted by the 3D EEI effect (~0.03%).

• The residual resistivities  $\rho_0(B1) = 73.9 \ \mu\Omega$  cm and  $\rho_0(B2) = 75.0 \ \mu\Omega$  cm differ by  $\approx 1\%$ . The 3D EEI effect predicts a  $\approx 3\%$  difference in resistivity increase. But, experiment shows  $\approx 50\%$  difference.

$$\frac{\Delta\rho(T)}{\rho(T_0)} = -\frac{0.915e^2}{4\pi^2\hbar} \left(\frac{4}{3} - \frac{3}{2}\tilde{F}\right)\rho(T_0)\sqrt{\frac{k_B}{\hbar D}} \left(\sqrt{T} - \sqrt{T_0}\right)$$

 $\approx 3 \times 10^{-4}$  in our MO<sub>2</sub> nanowires

Independence of applied magnetic field of the resistivity increase is in accord with nonmagnetic orbital 2CK effect !

#### 10/24/2019

**Crystal Structure of MO**<sub>2</sub> & Oxygen Vacancies

Oxygen vacancies lead to an almost perfect  $C_4$ -symmetry around the transition metal ions M1 & M2 next to the vacant site:



(courtesy of S. Kirchner)

\* Stefan Kirchner \*

# **Orbital two-channel Kondo effect in MO**<sub>2</sub>



- Every oxygen vacancy generates two *defect electrons* due to charge neutrality.
- Coulomb repulsion forces the *defect electrons* to localize at different transition metal ion sites near the vacancy site.
- For Ir-ions in  $IrO_2$ : 5d-shell is half-filled
- The defect electron at M2 (M1) can localize in the  $d_{xz}$ -orbital or  $d_{yz}$ -orbital
  - equivalent to spin-up and spin-down state orbital Kondo effect
- Spin-degenerate conduction band: two independent scattering channels

#### **Orbital two-channel Kondo effect**

10/24/2019

\* Stefan Kirchner \*

(courtesy of S. Kirchner)

## Heuristic picture for electron-quantum impurity scattering



Elastic electron-impurity scattering  $\Rightarrow$  "residual resistivity"



Magnetic spin-flip scattering

 $\Rightarrow$  Standard 1CK effect

**S** =±1/2 degenerate doublet states



#### **Electron-quantum impurity scattering:**

The quantum impurity  $M^{+3}$  contains a defect electron which tunnels between the two-fold degenerate  $d_{xz}$  and  $d_{yz}$  orbitals.

The spin-up and spin-down conduction electrons act as two independent and equivalent channels.

 $\Rightarrow$  Nonmagnetic orbital 2CK effect !

# **Transport anomalies in MO**<sub>2</sub>

#### Can we test that model?

Lifting the spin degeneracy would lead to an orbital one-channel Kondo effect

 $\rightarrow$  study anti-ferromagnetic RuO<sub>2</sub> (same structure as IrO<sub>2</sub>)

In RuO<sub>2</sub> the 4d<sub>xz</sub> and 4d<sub>yz</sub> orbitals are half filled while the  $4d_{x^2-y^2}$  orbital is located well below the Fermi energy and is completely filled. [Berlijn et al. "Itinerant antiferromagnetism in RuO<sub>2</sub>" Phys.Rev.Lett. (2017)]



\* Stefan Kirchner \*

(courtesy of S. Kirchner)

#### The low-T resistance increase is insensitive to large magnetic fields !





T. A. Costi, PRL 85, 1504 (2000)

Lien et al., PRB 84, 155432 (2011)

# **Transport anomalies in MO**<sub>2</sub>

#### Orbital one-channel Kondo effect in anti-ferromagnetic RuO<sub>2</sub>



Single-channel Kondo scaling over three decades in  $T/T_{K}$  !

T<sub>K</sub> values vary from 3 to 80 K. The Kondo resistivities conform to the universal 1CK scaling function !

Oxygen vacancies drive an orbital one-channel Kondo effect in RuO<sub>2</sub>!

(courtesy of S. Kirchner)



## Ruling out 3D electron-electron interaction effect

• Conformation to the one-channel Kondo scaling form for three decades in  $T/T_{\kappa}$  rules out the 3D EEI effect

• The observed resistivity increase is more than one order of magnitude as would be expected from the 3D EEI effect

$$\frac{\Delta\rho(T)}{\rho(T_0)} = -\frac{0.915e^2}{4\pi^2\hbar} \left(\frac{4}{3} - \frac{3}{2}\tilde{F}\right)\rho(T_0)\sqrt{\frac{k_B}{\hbar D}} \left(\sqrt{T} - \sqrt{T_0}\right)$$

 $\approx 3 \times 10^{-4}$  in our MO<sub>2</sub> nanowires

The insensitivity to applied magnetic field indicates nonmagnetic orbital one-channel Kondo effect !

## Recent 2CK experiment of layered compound Zr-As-Se (?)

PRL 117, 106601 (2016)

PHYSICAL REVIEW LETTERS

week ending 2 SEPTEMBER 2016

#### Two-Channel Kondo Physics due to As Vacancies in the Layered Compound ZrAs<sub>1.58</sub>Se<sub>0.39</sub>

T. Cichorek and L. Bochenek

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wroclaw, Poland



in collaboration with MPI Dresden, Zhejiang University

For the layered compound  $ZrAs_{1.58}Se_{0.39}$ , the authors argue that vacancies in the square nets of As give rise to the low-*T* transport anomaly in line with the nonmagnetic version of the 2CK effect.

## Recent 2CK experiment of layered compound Zr-As-Se (?)

#### PRL 118, 259701 (2017)

#### PHYSICAL REVIEW LETTERS

#### week ending 23 JUNE 2017

#### Comment on "Two-Channel Kondo Physics due to As Vacancies in the Layered Compound ZrAs<sub>1.58</sub>Se<sub>0.39</sub>"

In a recent Letter [1], Cichorek *et al.* reported that a magnetic field independent  $AT^{1/2}$  term in the low-temperature resistivity of ZrAs<sub>1.58</sub>Se<sub>0.39</sub> could not be caused by electron-electron interaction (EEI) and could only be explained by a two-channel Kondo effect (2CKE). This statement was formulated on the basis of quantitative analysis of experimentally obtained *A*-coefficient values in light of the Altshuler-Aronov theory of EEI in disordered conductors [2]. The authors argue that even when the electron screening factor F = 0, the values of the *A* coefficient for samples 1 and 2 of single-crystalline ZrAs<sub>1.58</sub>Se<sub>0.39</sub> give unrealistic diffu-



#### PHYSICAL REVIEW B 97, 134201 (2018)

#### Origin of the $-|A|T^{1/2}$ term in the resistivity of disordered ZrAs<sub>1.58</sub>Se<sub>0.39</sub>

Daniel Gnida

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## 3D electron-electron interaction effect in Ti-Al alloys



Resistivity increase for Al-doped Ti alloys with  $\rho_0$  = 143, 167 and 204 µm cm.

Phys. Rev B 48, 5021 (1993)







## CONCLUSION

- IrO<sub>2</sub> and RuO<sub>2</sub> crystalize in the rutile structure, with approximate C<sub>4</sub> symmetry. Properties of the C<sub>4</sub> group imply two-fold degeneracy of the nonmagnetic impurity.
- In paramagnetic IrO<sub>2</sub>, the spin-degeneracy of the conduction bands is preserved. ⇒ Orbital 2CK effect !
- In antiferromagnetic RuO<sub>2</sub>, the conduction band is (locally) spinpolarized. ⇒ Orbital 1CK effect !
- The symmetries that that enforces the existence of Dirac nodal lines also promote the formation of non-magnetic Kondo correlation.
- Both the emergence of the strange metallic state that accompanies unconventional superconductivity and the formation of the 2CK effect originate from strong electron interactions.

A quantum impurity (a localized spin, a moving electron or atom, etc.) with internal degree of freedom (two-fold degeneracy) generates the Kondo effect. Kondo, 1976 Nozieres, 1980 Zawadowski, 1980s Many more .....