



TAILORING THE CRYSTAL STRUCTURE TOWARD OPTIMAL SUPERCONDUCTORS

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06/23/2016
Final Report

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1. REPORT DATE (DD-MM-YYYY) 14-06-2016		2. REPORT TYPE final		3. DATES COVERED (From - To) 2011-2016		
4. TITLE AND SUBTITLE TAILORING THE CRYSTAL STRUCTURE TOWARD OPTIMAL SUPERCONDUCTORS				5a. CONTRACT NUMBER FA9550-11-1-0023		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Emilia Morosan				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rice University 6100 Main Street MS 61 Houston TX 77005				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 North Randolph Street Suite 325, Room 3112 Arlington VA, 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT approved for public release						
13. SUPPLEMENTARY NOTES NA						
14. ABSTRACT We have studied the properties of layered transition metal compounds in search of unconventional superconductors. The aim is to identify ground states competing with superconductivity, and to use tuning parameters such as doping or pressure, to reveal the effects of this competition. The key results from the project are: - the discovery of remarkable transport properties in the doped layered dichalcogenide TiSe ₂ , where Pt doping or Se deficiency result in a 10 order of magnitude change in the low temperature resistivity. - the synthesis and characterization of single crystals of GeBi ₂ Te ₄ , where the proper structural characterization revealed the non-trivial topological metal properties of this compound - the discovery of remarkably high ordering temperature (up to 300 K) in R ₅ Pb ₃ compounds (R = heavy rare earth) - the discovery of enhanced itinerant magnetism in Co ₂ As _{1-x} P _x , with the magnetic properties tuned by structural phase transitions.						
15. SUBJECT TERMS superconductivity, magnetism						
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TAILORING THE CRYSTAL STRUCTURE TOWARD OPTIMAL SUPERCONDUCTORS

- **Transition metal d^6 orbital compounds: Co_2As**

We explored the correlations between the magnetic and structural properties of Co_2As . Isoelectronic doping on the pnictogen site has revealed complex magnetism (Fig. 1-2) correlated with structural phase transitions. Instead of suppressing the AFM state of CoAs , P-doping in $\text{Co}_2\text{As}_{1-x}\text{P}_x$ enhances the magnetization for low x values ($x < 0.04$), followed by an itinerant ferromagnetic state (IFM) at intermediate x values ($0.04 \leq x \leq 0.85$) and an enhanced Pauli paramagnetic state for $x > 0.95$.

Fig. 1. $\text{Co}_2\text{As}_x\text{P}_x$ (a) lattice parameters as a function of P content x . (b-e) Magnetic susceptibility for three composition ranges, corresponding to a spin fluctuating ferromagnetic state (b), an itinerant ferromagnetic region (c-d) and a Stoner enhanced paramagnetic state (e).

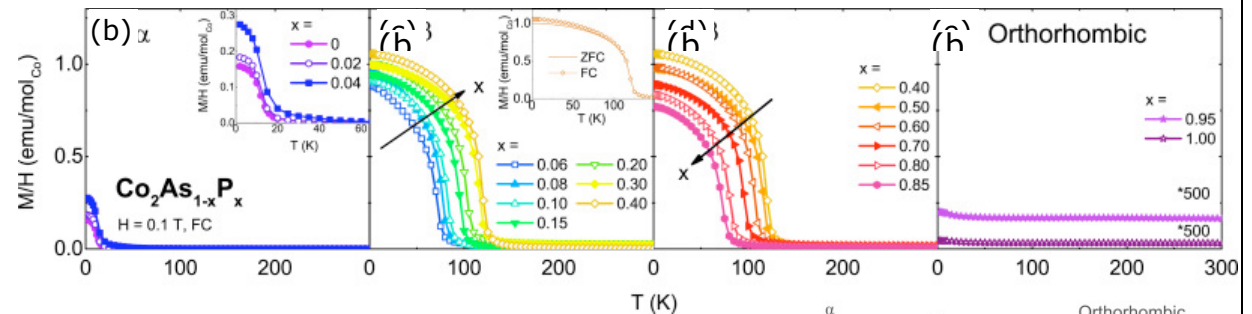
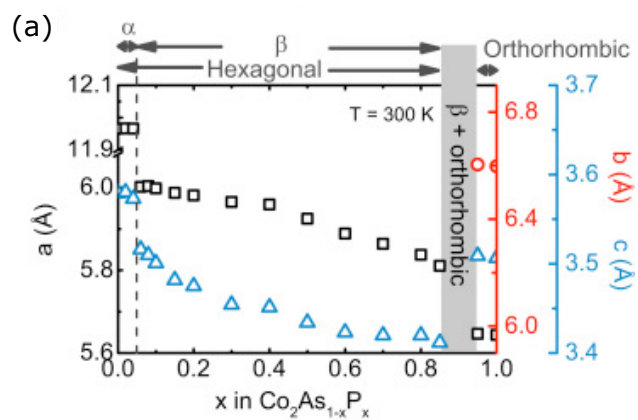
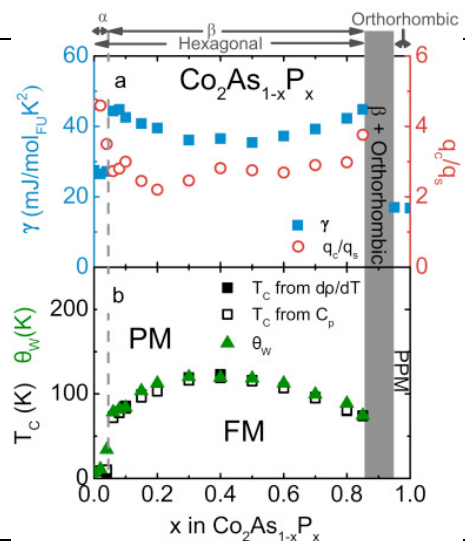


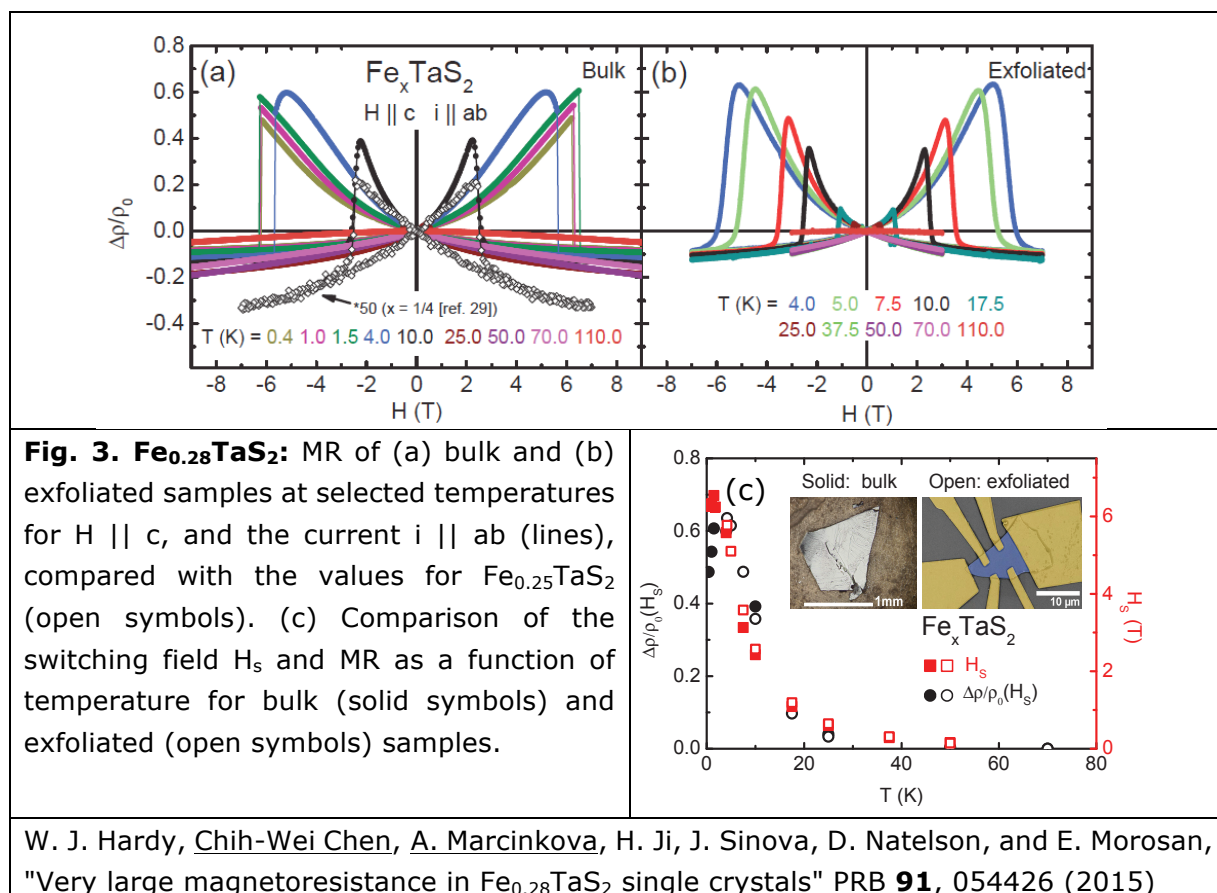
Fig. 2: $\text{Co}_2\text{As}_{1-x}\text{P}_x$ (a) Electronic specific heat coefficient γ and the Rhodes–Wohlfarth ratio q_d/q_s . (b) Phase diagram of $\text{Co}_2\text{As}_{1-x}\text{P}_x$: T_C and Weiss-temperature (θ_w) as a function of composition x . For $0.04 \leq x \leq 0.85$, the compounds are in the hexagonal phase and exhibit ferromagnetic behavior (FM). Above T_C , compounds show Curie–Weiss-like paramagnetism (CWPM). For $0.95 \leq x \leq 1$, the compounds show Pauli paramagnetism (PPM). The gray region indicates the mixed phases region.



Chih-Wei Chen, Jiakui K. Wang and Emilia Morosan, Physica B **481**, 236 (2015)

- **Large magnetoresistance in intercalated transition metal dichalcogenides: $\text{Fe}_{0.28}\text{TaS}_2$**

Magnetic moments intercalated into layered transition metal dichalcogenides are an excellent system for investigating the rich physics associated with magnetic ordering in a strongly anisotropic, strong spin-orbit coupling environment. We examined the electronic transport and magnetization in $\text{Fe}_{0.28}\text{TaS}_2$, a highly anisotropic ferromagnet with a Curie temperature of ~ 68.8 K. Despite an ordering temperature nearly half that in the superstructure analogue $\text{Fe}_{0.25}\text{TaS}_2$, $\text{Fe}_{0.28}\text{TaS}_2$ showed a remarkably large magnetoresistance $\text{MR} \sim 60\%$, a nearly two orders of magnitude increase from the $\text{MR} \sim 1\%$ in the ordered compound. Both the magnetization and transport properties are nearly insensitive to the sample thickness down to $\sim 100\text{nm}$. The anomalous Hall data confirmed a dominance of spin-orbit coupling in the magnetotransport properties of this material, correlated with the large MR, much larger than the typical values for bulk metals, and comparable to state-of-the-art giant MR in thin film heterostructures, and smaller only than colossal MR in Mn perovskites or high mobility semiconductors. After considering alternative scenarios (AMR or an analog of GMR due to domain structures), we argued that the large MR was due to spin-disorder scattering in the strong spin-orbit coupling environment, and suggested that this could be a design principle for materials with large MR.



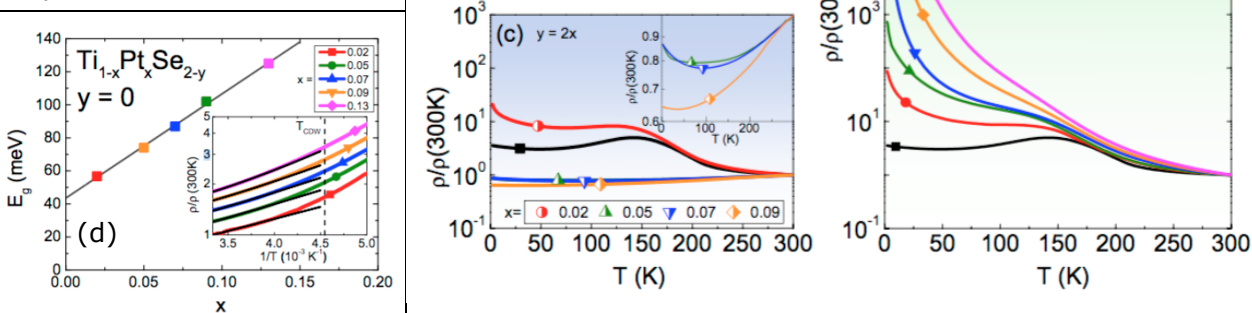
W. J. Hardy, Chih-Wei Chen, A. Marcinkova, H. Ji, J. Sinova, D. Natelson, and E. Morosan, "Very large magnetoresistance in $\text{Fe}_{0.28}\text{TaS}_2$ single crystals" PRB **91**, 054426 (2015)

- **Chemical tuning of electrical transport in $\text{Ti}_{1-x}\text{Pt}_x\text{Se}_{2-y}$**

Intercalation of TiSe_2 with various non-magnetic transition metals pointed to very complex electrical transport properties in this system, including multiple charge density wave transitions, superconductivity etc. We used chemical control parameters to study their effects on the transport properties of TiSe_2 .

In addition to intercalation, doping and chalcogen deficiency are possible chemical tuning parameters in these systems. We focused on the effects of Pt substitution for Ti and Se deficiency, separately and together, in $\text{Ti}_{1-x}\text{Pt}_x\text{Se}_{2-y}$. The resulting electrical resistivity was found to vary over more than 10 orders of magnitude between the most insulating state (when $x > 0$, $y=0$) to the most metallic state ($y > 0$): Se deficiency ($y > 0$) increased the metallic character of TiSe_2 , while a large increase of the low-temperature resistivity was favored in the stoichiometric ($y = 0$) system with intercalated Pt ($x > 0$). The chemical tuning of the resistivity in $\text{Ti}_{1-x}\text{Pt}_x\text{Se}_{2-y}$ with Se deficiency *and* Pt doping resulted in a metal-to-insulator transition. Simultaneous Pt doping and Se deficiency ($x, y > 0$) confirmed the competition between the two opposing trends in electrical transport, with the main outcome being the suppression of the charge density wave transition below 2 K for $y = 2x = 0.18$. Band structure calculations on a subset of $\text{Ti}_{1-x}\text{Pt}_x\text{Se}_{2-y}$ compositions were in line with the experimental observations.

Fig. 4: $\text{Ti}_{1-x}\text{Pt}_x\text{Se}_{2-y}$ Scaled electrical resistivity for (a) $x = 0$ (no Pt), (b) $y = 0$ (no Se deficiency), and (c) $y = 2x$. (d) The high temperature gap increases monotonously with increasing amounts of doped Pt.

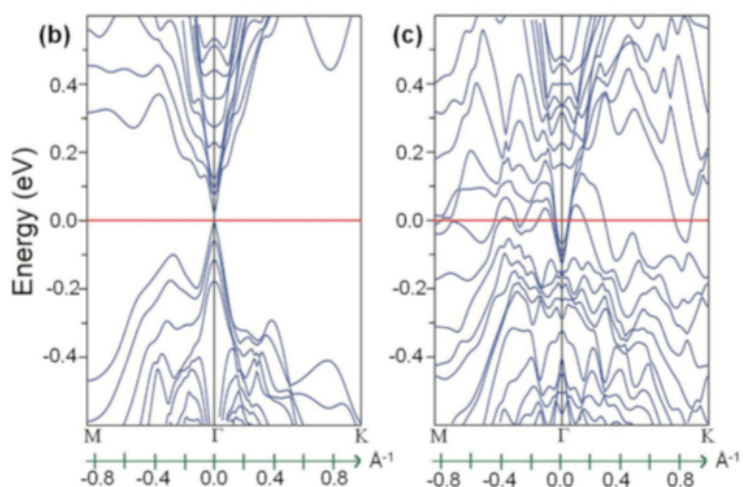


Justin S. Chen, Jiakui K. Wang, Scott V. Carr, Sven C. Vogel, Olivier Gourdon, Pengcheng Dai and E. Morosan, PRB **91**, 045125 (2015)

- **Topological metal behavior in GeBi_2Te_4 single crystals**

Pseudobinary chalcogenide compounds such as $\text{Bi}_2\text{Se}_2\text{Te}$ (BiTe-BiSe_2) or GeBi_2Te_4 ($\text{BeTe-Bi}_2\text{Te}_3$) have been theoretically predicted to be 3D topological insulators. In particular the latter compound posed an unresolved controversy, given that ARPES measurements indicated the presence of a Dirac point below the Fermi energy, while first principle calculations placed the Dirac point inside the gap. Our study on high quality single crystals revealed a small structural distortion of the Ge octahedral, which has a great impact on the Fermi surface topology. The result is the shift of the Dirac point below the Fermi level, rendering GeBi_2Te_4 as a nontrivial topological metal, in agreement with the ARPES results.

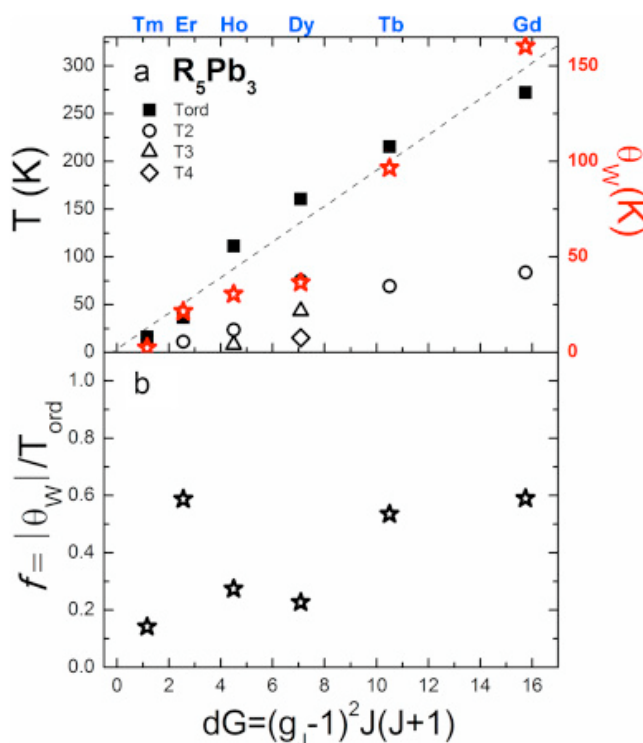
Fig. 5 GeBi_2Te_4 : Calculated band structure based on the calculated (left) and experimental (right) structural models.



A. Marcinkova, J. K. Wang, C. Slavonic, Andriy H. Nevidomskyy, K. F. Kelly, Y. Filinchuk and E. Morosan, PRB **88**, 165128 (2013)

- **Strong magnetic coupling in the hexagonal $R_5\text{Pb}_3$ compounds ($R = \text{Gd-Tm}$):** Remarkably high ordering temperatures were found in the $R_5\text{Pb}_3$ compounds, with Curie temperature close to room temperature in the $R = \text{Gd}$ member of the series. For all $R_5\text{Pb}_3$ reported here the Weiss temperatures θ_W are several times smaller than the ordering temperatures T_{ORD} , which, together with the multiple magnetic transitions in most of these compounds, indicate very large anisotropic exchange and crystal electric fields.

Fig. 6: $R_5\text{Pb}_3$ Ordering and Weiss temperatures (top) together with their ratio (bottom) showing the unexpected θ_W up to five times smaller than the ordering temperature.



Andrea Marcinkova, Clarina de la Cruz, Joshua Yip, Liang L. Zhao, Jiakui K. Wang, E. Svanidze and E. Morosan, *J. Magn. Magn. Mater.* **384**, 192 (2015)

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FA9550-11-1-0023

Principal Investigator Name

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Emilia Morosan

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Reporting Period Start Date

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Reporting Period End Date

06/13/2016

Abstract

We have studied the properties of layered transition metal compounds in search of unconventional superconductors. The aim is to identify ground states competing with superconductivity, and to use tuning parameters such as doping or pressure, to reveal the effects of this competition. The key results from the project are:

- the discovery of remarkable transport properties in the doped layered dichalcogenide TiSe_2 , where Pt doping or Se deficiency result in a 10 order of magnitude change in the low temperature resistivity.
- the synthesis and characterization of single crystals of GeBi_2Te_4 , where the proper structural characterization revealed the non-trivial topological metal properties of this compound
- the discovery of remarkably high ordering temperature (up to 300 K) in R_5Pb_3 compounds (R = heavy rare earth)
- the discovery of enhanced itinerant magnetism in $\text{Co}_2\text{As}_{1-x}\text{Px}$, with the magnetic properties tuned by structural phase transitions.

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- W. J. Hardy, Chih-Wei Chen, A. Marcinkova, H. Ji, J. Sinova, D. Natelson, and E. Morosan, "Very large magnetoresistance in Fe_{0.28}TaS₂ single crystals" PRB 91, 054426 (2015)
- Justin S. Chen, Jiakui K. Wang, Scott V. Carr, Sven C. Vogel, Olivier Gourdon, Pengcheng Dai and E. Morosan, PRB 91, 045125 (2015)
- A. Marcinkova, J. K. Wang, C. Slavonic, Andriy H. Nevidomskyy, K. F. Kelly, Y. Filinchuk and E. Morosan, PRB 88, 165128 (2013)
- Andrea Marcinkova, Clarina de la Cruz, Joshua Yip, Liang L. Zhao, Jiakui K. Wang, E. Svanidze and E. Morosan, J. Magn. Magn. Mater. 384, 192 (2015)

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