

Session 9

Keynotes lectures

Ternary and Quaternary Rare-Earth Germanides: Discovery of Intermetallic Compounds from Traditional to Machine-Learning Approaches

Dong Zhang,^a Anton O. Oliynyk,^a Gabriel M. Duarte,^a Abishek K. Iyer,^a Taylor D. Sparks,^b
Leila Ghadbeigi^b & Arthur Mar^{*,a}

^a Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

^b Department of Materials Science and Engineering, University of Utah, Salt Lake City,
UT, USA 84112

Ternary rare-earth transition-metal germanides $RE-M-Ge$ represent a large group of intermetallic compounds that exhibit a rich structural chemistry and many interesting physical properties including superconductivity and magnetocaloric effects. Traditional approaches for materials discovery would involve systematic investigations of phase diagrams, or identification of structural motifs, such as MGe ladders and Ge_n bridges, to reveal patterns that permit new compounds to be targeted. A different and accelerated approach for materials discovery is through machine-learning techniques, which can be used to predict crystal structures or suggest promising candidates for desired physical properties.¹ We present here case studies of many new ternary (e.g., Ce–Rh–Ge) and quaternary (e.g., $RE_4M_2XGe_4$ where $X = Ag, Cd, In$) phases that were discovered through both approaches. In particular, we discuss how machine-learning approaches are valuable in guiding the search for intermetallics that exhibit low thermal conductivity, which is a key criterion for thermoelectric materials.

References

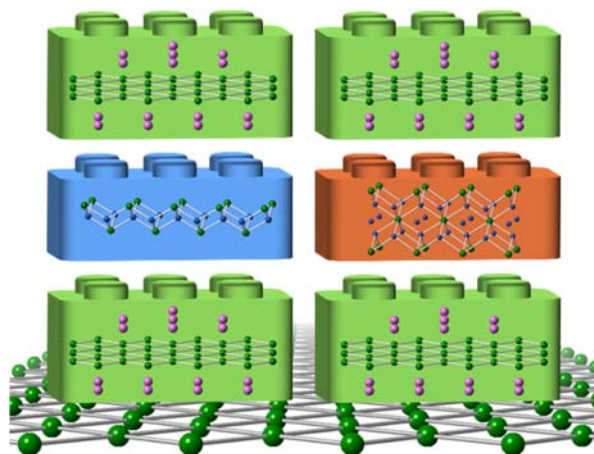
1. Oliynyk, A. O.; Mar, A. *Acc. Chem. Res.* **2018**, *51*, 59–68.

Adventures in Solid State Synthesis: Hidden Gems to Link Materials' Properties

Julia Chan

^a Department of Chemistry and Biochemistry, The University of Texas at Dallas, 800 W Campbell Road, Richardson, Texas, 75080, USA

The discovery and characterization of novel intermetallic compounds is important for broadening the understanding of structure-property relationships of magnetic materials. Our current research interests in superconductivity and unusual magnetism rely heavily on the intimate relationship between structure and physical properties. Likewise, the determination of anisotropic physical properties from high quality single crystals is vital in probing the intrinsic electrical and the competing magnetic interactions to understand the chemistry and physics of these materials. The discovery of novel magnetic and electronic properties in low-dimensional materials has led to the pursuit of hierarchical materials with specific substructures. Low-dimensional solids are highly anisotropic by nature and show promise in new quantum materials leading to exotic physical properties not realized in three dimensional materials. In this talk, I will highlight the crystal growth, characterization, and properties of germanides and stannides and layered antimonides and the potential for compounds in reduced dimensions.



References

1. Benavides, K.A.; Oswald, I.W.H.; Chan, J.Y., "Casting a Wider Net: Rational Synthesis Design of 2-Dimensional Bulk Materials", *Acc. Chem. Res.* **2018**, *1*, 51, 12–20

Coupled Valence and Spin State Transition in a class of Pr- and Co-based oxides.

Vincent HARDY^a, Yohann BREARD^a, and François GUILLOU^{a,b}

^aLaboratoire CRISMAT, UMR 6508, CNRS/ENSICAEN/NU, 6 Boulevard Marechal Juin, 14050 Caen, France.

^b Present address : Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Inner Mongolia Normal University, Hohhot 010022, China

Less than ten years ago, a peculiar type of interplay between the magnetism of 4f and 3d elements emerged in some oxides containing both Pr and Co [1]. This phenomenon yields a sharp transition having a first-order character and which strongly impacts all the physical properties, even though this transition does not correspond neither to a change in crystallographic structure nor to a magnetic ordering. Actually, this transition can be regarded as an unusual synergy between various electronic degrees of freedom, involving both “outer” electrons for Pr (valence state) and “inner” electrons for Co (spin state). More specifically, this coupled Valence and Spin State Transition (VSST) creates a link between the transformations $\text{Pr}^{3+} \leftrightarrow \text{Pr}^{4+}$ and $\text{Co}^{3+} (\text{High Spin}) \leftrightarrow \text{Co}^{3+} (\text{Low Spin})$. We have suggested that the coupling between these “electronic states” can be interpreted as a result of effects of chemical pressure [2].

In this lecture, we will first present the main experimental features of this VSST within the series $(\text{Pr}_{1-y}\text{Sm}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$, before suggesting an attempt of modelization. Our phenomenological approach will be based on a combination of the “theory of regular solutions” (for the spin-state transition) and the “interconfigurational fluctuation model” (for the valence transition) [3]. It will be compared to experimental data, in particular the evolution of the populations of the different species involved in the VSST, that were derived from XAS (X-ray Absorption Spectroscopy) and XMCD (X-ray Magnetic Circular Dichroism) experiments.

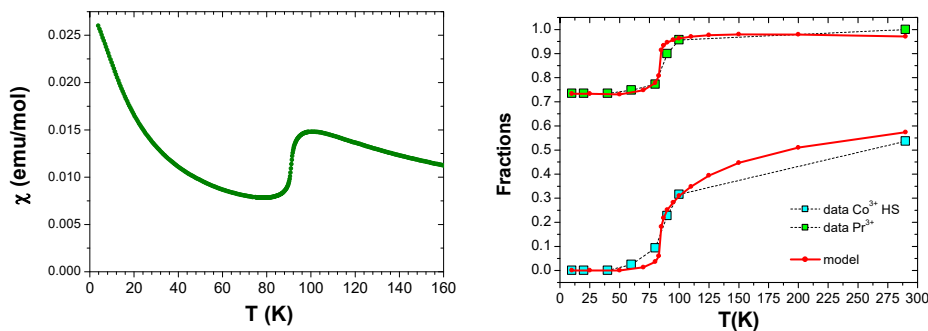


Figure 1. Left: Magnetic susceptibility of $(\text{Pr}_{1-y}\text{Sm}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ for $y=0.3$; Right: temperature dependence of the ratios Pr^{3+}/Pr and $\text{Co}^{3+} (\text{HS})/\text{Co}^{3+}$ (XAS data and calculations).

[1]. A. J. Barón-González et al., Phys. Rev. B 81, 054427 (2010); J. Hejtmánek et al., Phys. Rev. B 82, 165107 (2010); J. L. García-Muñoz et al., Phys. Rev. B 84, 045104 (2011); J. Herrero-Martín, Phys. Rev. B 84, 115131 (2011).

[2] F. Guillou et al., Phys. Rev. B 87, 115114 (2013); V. Hardy et al., J. Phys. Cond. Matt. 25, 246003 (2013); F. Guillou et al., Phys. Rev. B 95, 174445 (2017).

[3] Zimmermann et al., J. Phys. Chem. Solids 38, 779 (1977); Franz et al., Phys. Rev. Lett. 45, 64 (1980); Croft et al., Phys. Rev. Lett. 48, 826 (1982).

Session 9

Invited lectures

MAGNETOPHORESIS OF MAGNETOMIGRATION IN AQUEOUS LANTHANIDE SOLUTIONS

Isadora R. Rodrigues,^{a*} Liubov Lukina,^a Sam Dehaeck,^b Pierre Colinet,^b Koen Binnemans,^c & Jan Fransaer^a

^a Department of Material Engineering, KU Leuven, Kasteelpark Arenberg 44, P.O. Box 2450, B-3001 Heverlee, Belgium

^b Université Libre de Bruxelles (ULB), TIPs (Transfers, Interfaces and Processes), CP 165/67, Av. F. D. Roosevelt 50, 1050 Brussels, Belgium

^c Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Box 2404, B-3001 Heverlee, Belgium

This work studies the *magnetomigration* of trivalent lanthanide ions (Ln^{3+}) and the *magnetophoresis* of droplets containing Ln^{3+} ions. Magnetomigration and magnetophoresis are used to distinguish the motion of ions and small molecules from larger particles through a medium due to the presence of an external magnetic field. Hydrophilic droplets of concentrated aqueous Ln^{3+} solutions suspended in a hydrophobic medium develop different velocities when subjected to a magnetic field. The droplets undergo a “*magnetophoretic sprinting*” and their velocities are correlated to the magnetic susceptibility of the Ln^{3+} ions present in the droplet. The magnetophoretic motion of droplets of strongly paramagnetic Ln^{3+} ions was considerably faster compared to that of droplets of weakly paramagnetic ones. Droplets containing diamagnetic ions (La^{3+} and Lu^{3+}) were not affected by the magnetic field. When the velocity was plotted as a function of the atomic number, a binodal-shaped curve was obtained, similar to that of the effective magnetic moments. This shape reflects changes of the magnetic susceptibility across the lanthanide series. In recent studies, Mach-Zehnder interferometry (MZI) was used to investigate the magnetomigration of Dy^{3+} ions in aqueous solutions.¹ Despite these recent reports, the magnetically induced motion of small molecules and ions is still controversial. Brownian motion of ions at room temperature should overpower the magnetomigration of the ions.² To validate this, a careful experiment was performed in which a homogenous Dy^{3+} solution was exposed to an external magnetic field. No migration of ions was detected.³ However, when a concentration gradient was introduced in the solution by solvent evaporation, consistent migration of paramagnetic Dy^{3+} ions was observed. This is an important observation to explain the mechanism of the magnetic motion of ions described in the literature.^{1,3-4}

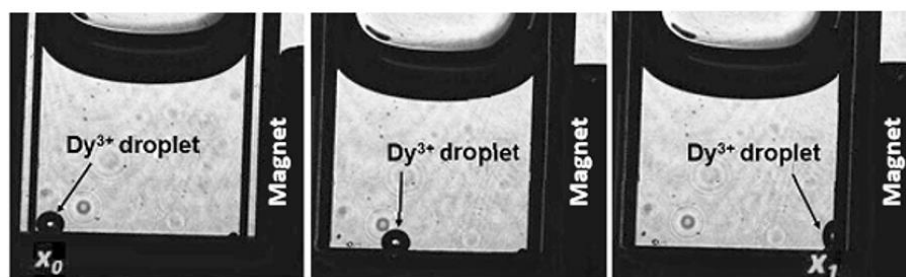


Figure 1. Magnetophoresis of a Dy^{3+} -containing droplet inside paraffin oil.

References

1. Lei, Z.; Fritzsche, B.; Eckert, K. Evaporation-Assisted Magnetic Separation of Rare-Earth Ions in Aqueous Solutions. *J. Phys. Chem. C* **2017**, 121, 24576–24587.
2. Coey, J. Magnetism and Magnetic Materials; Cambridge University Press: Cambridge, United Kingdom, **2010**.
3. Rodrigues, I.; Lukina, L.; Dehaeck, S.; Colinet, P.; Binnemans, K.; Fransaer, J. Magnetomigration of Rare-Earth Ions Triggered by Concentration Gradients. *J. Phys. Chem. Lett.* **2017**, 8, 5301–5305.
4. Fujiwara, M.; Mitsuda, K.; Tanimoto, Y. Movement and Diffusion of Paramagnetic Ions in a Magnetic Field. *J. Phys. Chem. B* **2006**, 110, 13965–13969.

Lutetium Trigermanide LuGe₃: High-Pressure Synthesis, Chemical Bonding and Superconductivity

*Julia-Maria Hübner, Matej Bobnar, Lev Akselrud, Yurii Prots, Yuri Grin, Ulrich Schwarz**

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany

The element semiconductors silicon or germanium form a rich variety of binary phases with electropositive partners of the alkaline-, alkaline earth- and rare earth metal groups. These compounds often exhibit significant contributions of classical covalent two-center two-electron and ionic interactions, whereby chemical bonding and electron count normally follow the principles established by the Zintl-Klemm concept [1].

Although, compounds violating these electron counting rules or possessing unusual coordination environments in the covalent partial structure of the p-block element, often possess remarkable properties, like superconductivity. The application of high-pressure methods is one strategy to obtain such phases.

A systematic study of tetrel connectivities exceeding the scope of the 8-N rule revealed the special suitability of the structure MTt_3 ($M = Y, La, Eu, Ho, Yb, Lu$; $Tt = Si, Ge$) [2-7] for obtaining interesting physical properties. Among the series of rare-earth metals, lutetium, normally occurring as Lu^{3+} in the bound state, provides absence of a magnetic moment, setting the stage for the occurrence of phonon-mediated superconductivity in these so-called covalent metals. Hitherto, the superconducting $LuSi_3$ [6] has been described, but no analogue phases are known in the system Lu-Ge.

The new metastable binary compound $LuGe_3$ has been synthesized under high-pressure, high-temperature conditions at pressures between 8(1) and 14(2) GPa and temperatures in the range of 1100(150) to 1500(150) K.

The atomic arrangement of $LuGe_3$ is isotypic to $DyGe_3$, containing double layers of condensed Ge_2 dumbbells as well as Ge zig-zag chains, with the space group $Cmcm$ and the lattice parameters $a = 3.97547(3)$ Å, $b = 20.3771(2)$ Å and $c = 3.86966(3)$ Å. Chemical bonding analysis reveals multicentre polar interactions between Lu and Ge, as well as a lone pair on each Ge. A transition into a BCS-type superconducting state below $T_c = 3.3(3)$ K is indicated by magnetic susceptibility, specific heat, and electrical conductivity measurements.

References

- [1] Demchyna, R.; Leoni, S.; Rosner, H.; Schwarz, U. *Z. Kristallogr.* **2006**, 221, 420-434.
- [2] Fukuoka, H.; Suekuni, K.; Onimaru, T.; Inumaru, K. *Inorg. Chem.* **2011**, 50, 3901-3906.
- [3] Meier, K.; Cardoso-Gil, R.; Schwarz, U. *Z. Kristallogr.* **2011**, 226, 297-298.
- [4] Wosylus, A.; Prots, Yu.; Schwarz, U. *Z. Kristallogr. NCS* **2011**, 226, 295-296.
- [5] Harada, M.; Fukuoka, H.; Matsumura, D.; Inumaru, K. *J. Phys. Chem. C* **2012**, 116, 2153-2158.
- [6] Schwarz, U.; Wosylus, A.; Rosner, H.; Schnelle, W.; Ormeci, A.; Meier, K.; Baranov, A.; Nicklas, M.; Leipe, S.; Müller, C.J.; Grin, Yu. *J. Am. Chem. Soc.* **2012**, 134, 13558-13561.
- [7] Castillo, R.; Baranov, A.; Burkhardt, U.; Grin, Yu.; Schwarz, U. *Z. Anorg. Allg. Chem.* **2015**, 641(2), 355-361.

Session 9

Posters

Novel Heavy Fermion Compound

E. Svanidze,¹ A. Amon¹, M. Nicklas¹, A. Leithe-Jasper¹, Yu. Grin²

¹ *Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Strasse 40, 01187 Dresden, Germany, email: svanidze@cpfs.mpg.de*

The field of heavy fermion physics emerged nearly four decades ago and has since become one of the central research directions of condensed matter physics. While significant progress has been made in understanding heavy fermion behavior and accompanying phenomena, the global trends remain unclear. One of the avenues in the search for heavy fermion materials has focused on compounds with high coordination, and, therefore, low concentration of uranium atoms. This approach has proven fruitful in the case of antiferromagnetic U_2Zn_{17} and UCd_{11} , as well as unconventional superconductor UBe_{13} . The two former compounds are also the only two U-based canonical heavy fermion compounds. In this work, we present the discovery of $U_{11}Hg_{45}$ - the second heaviest and the third canonical U-based heavy-fermion compound. This compound exhibits an antiferromagnetic transition at $T_N = 2$ K, which can be suppressed by application of magnetic field, but not by pressure. A high value of the Sommerfeld coefficient $\gamma = 630$ mJ/U mol K^2 is likely related to the high itineracy of the f -electrons, as evidenced by the small entropy of the antiferromagnetic transition ($S_m = 0.15R\ln 2$). However, a large effective magnetic moment $\mu_{eff} = 3.43 \mu_B/U$ points to a local moment scenario. These features altogether advocate dual nature of $5f$ electrons in $U_{11}Hg_{45}$.