What we can learn from ^{1}H-NMR in metal hydrides at mega-bar pressures?

T. Meier[1]*, F. Trybel[1], S. Khandarkhaeva[1], G. Steinle-Neumann[1], S. Chariton[1], T. Fedotenko[2], S. Petitgirard[3], M. Hanfland[4], K. Glazyrin[5], N. Dubrovinskaia[2] and L. Dubrovinsky[1]

[1]*Bavarian Geoinstitute, University of Bayreuth, Bayreuth, Germany*
[2] *Material Physics and Technology at Extreme Conditions, Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany*
[3]*Institute of Geochemistry and Petrology, Department of Earth Sciences, Eidgenössische Technische Hochschule Zürich, Switzerland*
[4]*European Synchrotron Radiation Facility (ESRF), Grenoble Cedex, France*
[5]*Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*

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*e-mail: thomas.meier@uni-bayreuth.de

Hydrides and hydrogen-rich compounds attract considerable attention as the search for effective and "green energy" materials intensifies. Recent theoretical, computational and experimental results indicate that hydrides may hold the key to a deep understanding of high-temperature superconductivity and the synthesis of compounds exhibiting high critical temperatures.

A systematic analysis of computational results suggests that two properties are particularly important for achieving high-T_c superconductivity in metallic hydrides: (1) significant contribution of hydrogen to the electronic density of states at the Fermi energy (E_F), and (2) strong effects of hydrogen vibrations on the electronic structure of the material (i.e. electron-phonon coupling). Unfortunately, the lack of experimental methods in high pressure research able to access the electronic states of hydrogen in metal hydrides at extreme pressures has prohibited a direct confirmation of this hypothesis.

Recent developments in our group led to the implementation of Nuclear Magnetic Resonance (NMR) spectroscopy in diamond anvil cells at pressures approaching the megabar regime using magnetic flux tailoring Lenz lenses [1,2]. NMR spectroscopy is widely recognized for its sensitivity to hyperfine electronic interactions. In particular, Knight shift measurements provide a well-established technique to investigate the density of states of conduction electrons at the Fermi energy, enabling detection of deviations from free electron gas behavior or even electronic topological transitions of the Fermi surface and providing direct evidence of the Meissner-Ochsenfeld effect in the metal's superconducting state.

Here, we present the results of our first ^{1}H-NMR experiments on iron- and copper-hydrides which can be considered ideal test systems for this novel method due to the ease of *in-situ* sample synthesis as well as well defined crystal structures providing the possibility to closely control the hydrogenation of the samples.

While the observable electronic properties, i.e. Hydrogen Knight shift K_H and Jahn-Teller type relaxation

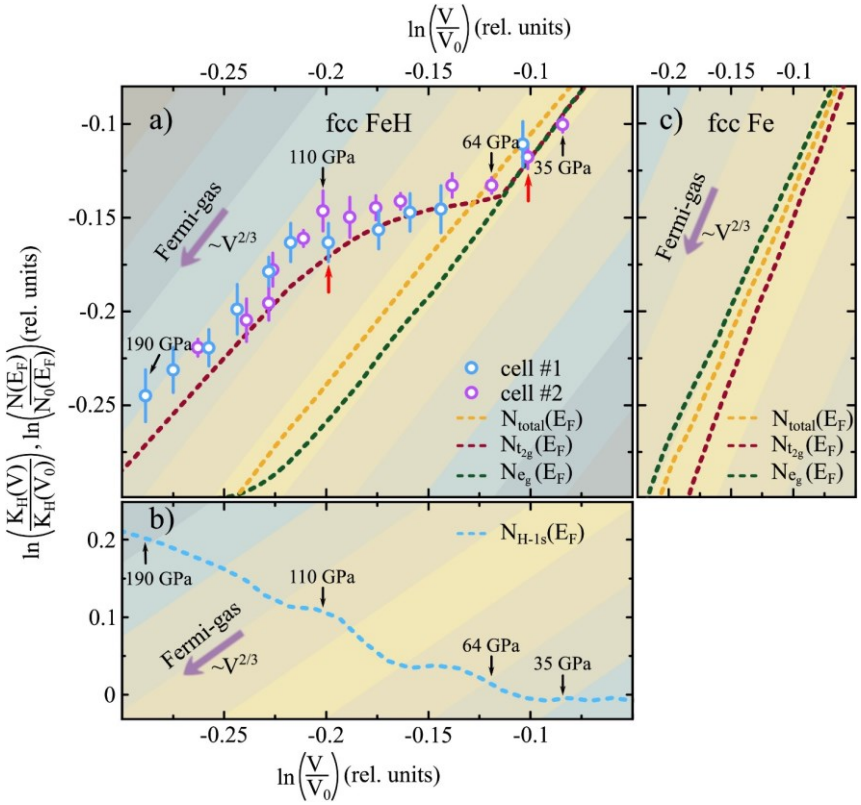

Figure: Comparison of experimental data and *ab-initio* electronic DOS calculations. a) Double logarithmic power plot of relative changes in K_H and the electronic density of states at the Fermi energy, $N(E_F)$, as a function of relative volume. The dashed lines show the dependence of $N_{total}(E_F)$, $N_{t2g}(E_F)$ and $N_{eg}(E_F)$. The diagonal color strips are guides to the eyes depicting a $\propto V^{2/3}$ scaling for free electron Fermi-gas like behavior. Black arrows denote respec-tive pressures points; red arrows show data recorded under decompression. b) Evolution of $N_{H\text{-}1s}(E_F)$. Indicated pres-sure markers are related to the experi-mental data points from a). c) Pressure dependence

rates R_1, clearly demonstrate metallic behavior in fcc FeH between 30 and 60 GPa (see figure), we observe a clear deviation from the expected Knight shift curvature between 60 and 110 GPa and a re-occurrence of a metallic $\propto V^{2/3}$ dependence of K_H approaching 200 GPa. Using *ab-initio* calculations, we could demonstrate that the iron metal's outermost partially uncompensated *3d* - t_2g orbital contributes to the formation of an intercalating sublattice of free-electron gas connecting hydrogen atoms, increasing their contribution to the electronic density of states at the Fermi energy [3]. Similar experiments in the copper-hydrogen system, in particular *hcp* Cu_2H up to 96 GPa and *fcc* CuH at pressures well above 100 GPa, further confirm these findings and provide the possibility to compare different hydrogenations.

Combining results of all investigated systems, a dominant NMR line narrowing mechanism was identified coinciding well with the formation of the hydrogen free electron sublattice [4].

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References:

[1] T. Meier, S. Khandarkhaeva, S. Petitgirard, T. Körber, A. Lauerer, E. Rössler, and L. Dubrovinsky, J. Magn. Reson. **292**, 44 (2018).

[2] T. Meier, S. Petitgirard, S. Khandarkhaeva, and L. Dubrovinsky, Nat. Commun. (2018).

[3] T. Meier, F. Trybel, S. Khandarkhaeva, G. Steinle-Neumann, S. Chariton, T. Fedotenko, S. Petitgirard, M. Hanfland, K. Glazyrin, N. Dubrovinskaia, and L. Dubrovinsky, Phys. Rev. X. (under Rev. (2019).

[4] T. Meier, F. Trybel, G. Criniti, S. Khandarkhaeva, E. Koemets, T. Fedotenko, K. Glazyrin, G. Steinle-Neumann, N. Dubrovinskaia, and L. Dubrovinsky, in preparation, (2019).