Intermetallic semiconductor $FeGa_3$ and related compounds: from chemical bonding to thermoelectricity and quantum criticality

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Bonding analysis on $FeGa_3$ reveals considerable Fe–Fe and Fe–Ga interactions, whereas a reexamination of its crystal structure shows strong anisotropy of Ga displacement parameters with additional structure features [1]. Ga-NQR experiments on $FeGa_{3-x}Ge_x$ detect localized antiferromagnetic Kondo-like correlations at low doping level and critical ferromagnetic fluctuations at the critical point, while itinerant magnetism is detected on ESR experiments.

In previous studies at MPI CPfS, intermetallic semiconductors with a narrow band gap and the stoichiometric formula $T^{(8)}Tr_3$ ($T^{(8)}$ = transition metal group 8, *Tr* = gallium or indium) were investigated. Considering the electronic structure, a strong d(*T*)-p(*Tr*)–hybridization with a sharp gradient in the density of states near the Fermi level fulfils appropriate conditions for a high Seebeck coefficient. Hence, a systematical study on the thermoelectric properties of several intermetallic compounds and substitution derivatives of the $FeGa_3$ type was carried out.

In the $FeGa_3$ crystal structure type (space group $P4_2/mnm$, No. 136; Fig. 1a), Ga atoms form a tetra-capped trigonal double prism (ttdp) filled by Fe obeying the general formula $Fe_2Ga1_4Ga2_8$ by considering the two different Ga sites.

Analysis of the chemical bonding was performed in the ideal crystal structure of $FeGa_3$ and isotype compounds [2]. Observing the topology of the electron density and of ELI-D, the electron density displays bond-critical points between iron and all its 8 nearest gallium neighbours, and also at the midpoint of the Fe–Fe interconnection line (Fig. 1b) [1]. The main interactions in the ttdp unit are 4×(Fe–Ga1), 4×(short Fe–Ga2), 8×(long Fe–Ga2), and 1×(Fe–Fe). Counting each as a formal 2-centre 2-electron bond yields a total of 17 bonds, thus 34 valence electrons are necessary. In relation with the 18-electron rule, an electron count of 17 ve attributed to an Fe centre is consistent with the formation of an additional Fe–Fe bond. Contrasting the situation of the molecule $Fe_2(CO)_9$ with three bridging CO groups reminds of an alternative model with 3-centre bonding. Thus, an alteration of the 2-centre-2-electron model could also be expected for $FeGa_3$. To characterize the three-centre delocalization of a bond *A*–*B*, 3-centre delocalization indices (DI) and derived bond delocalization ratios *G*(*A*,*B*) were calculated and analyzed. Indeed, especially the longer Fe–Ga2 bonds bridging the Fe–Fe dumbbell display a significant degree of 3c-character with $G(\mathrm{Fe,Ga2})_{\mathrm{bridge}} = 0.62$ (cf. $G(\mathrm{H,H'}) = 1.0$ for H_3^+). The main 3-centre delocalization channels of these $\mathrm{Fe–Ga2_{bridge}}$ bonds turn out to be of 3c-DI $\delta(\mathrm{Fe,Ga2_{bridge},Ga1})$ and $\delta(\mathrm{Fe,\ Ga2_{bridge},Ga2})$ type. The occurrence of significant 3-centre DIs Fe–Ga–Ga' can be understood from the electron sharing demands of the Ga atoms.

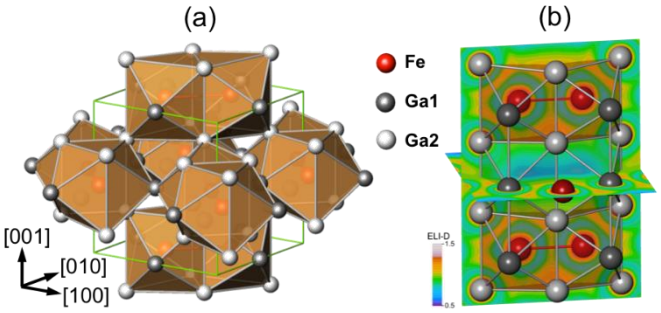

Fig.-1: a) Crystal structure of $FeGa_3$ with tetra-capped trigonal double prisms (ttdp) as main building block. b) ELI-D distribution in (1-10) and (001) planes showing ELI-D minima inside the empty ttdps.

The new crystal structure refinement of $FeGa_3$ reveals a strong anisotropy of the atomic displacement parameters ($U_{33} \approx U_{11} >> U_{22}$) for the Ga1 site. This local structure feature was also observed in $RuGa_3$, and may act as a phonon scattering centre. Further, the difference Fourier map shows a considerable residual electron density peak $\Delta\rho_{\max} = 2.92$ eÅ^{-3} allocated in the empty ttdp, formed between two filled ones. Interpreting this maximum as Fe, it results in a refined occupancy of ≈0.45 at.% for additional Fe in a first specimen (sample 1) and no additional Fe was detected in a second one (sample 2), corresponding to different prepared batches. This leads to a formulation of $Fe_{1+x}Ga_3$ with $0 \le x \le 0.018$ [1]. The minimal difference of Fe content with the ideal crystal structure is accounted experimentally by the magnetic behavior of the self-doped material $Fe_{1+x}Ga_3$. Magnetization measurements on sample 1 and 2 were conducted at 10 K. As result, sample 1 yielded a significantly higher saturation magnetization than sample 2 (Fig. 2a).

$FeGa_3$, like FeSi and $FeSb_2$, attracted great attention because of their nonmagnetic ground state and, as

already mentioned, their promising low temperature thermoelectric performance. Signatures of Kondo type of correlations are also found in these binary semimetals and considered in the context of correlated thermoelectrics.

Magnetic resonance is a very suitable microscopic tool for correlated matter on the verge of long range magnetic ordering and aims in particular to expose the real nature of the magnetic fluctuations [antiferromagnetic (afm) versus ferromagnetic (fm)] by temperature and field scaling.

Metallic behaviour and Fe-based magnetism could be introduced by controlled substitutions on the Fe or the framework site. For $FeGa_{3-x}Ge_x$, Ga nuclear quadrupole resonance (NQR) was performed to monitor the effect of Ge substitution across the phase diagram and to probe the magnetic fluctuations at zero magnetic field *via* the spin lattice relaxation rate (SLRR) through the QCP. In sum, absence of induced inhomogeneous lattice distortion (disorder), localized antiferromagnetic Kondo-like correlations at low doping levels, and critical ferromagnetic fluctuations at the critical point at the onset of fm order was observed [3]. The magnetic susceptibility of a single crystal on the verge of magnetism (x = 0.13), follows a $T^{-4/3}$ power law over a wide range in temperature, which confirms nicely the expected critical behaviour for this concentration by the bulk susceptibility. Noteworthily, this is unique for Fe-based intermetallic compounds where most frequently Fe impurities (in ppm scale) dominate the magnetic properties.

High quality single crystals of $FeGa_{3-x}Ge_x$ ($0 \leq x \leq 0.162$) were prepared and an electron spin resonance (ESR) study was performed, where ferromagnetic order is observed [4]. For $x = 0$, a well-defined ESR signal is registered, indicating the presence of preformed magnetic moments in the semiconducting phase. Upon Ge doping, the occurrence of itinerant magnetism clearly affects the ESR properties below ≈40 K, whereas at higher temperatures an ESR signal as seen in $FeGa_3$ prevails independent of the Ge content.

At high temperatures (>40K) the ESR spectra are *symmetric*, indicating a local-type ESR of Fe^{3+}-spins. In contrast, below ≈40 K (Fig. 2b), ESR spectra are observable only if Ga sites are substituted by Ge which leads to electron doping and itinerant magnetism. These low-temperature spectra are *asymmetric* which supports an itinerant type of resonance. Moreover, the linewidth strongly decreases with decreasing

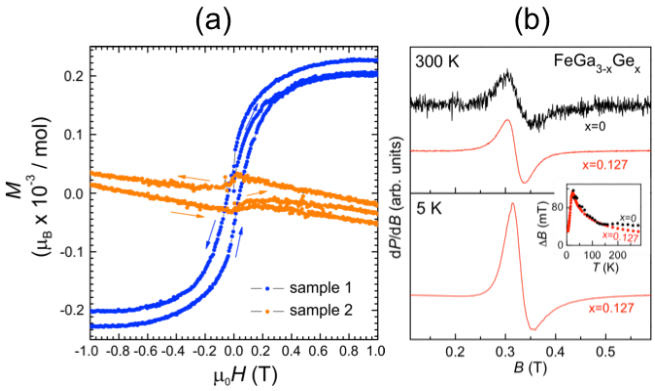

Fig.-2: a) Magnetization measurements at 10 K for $Fe_{1.018}Ga_3$ (sample 1) and $Fe_{1.00}Ga_3$ (samples 2). b) Derivative of the absorbed microwave power P vs. magnetic field B of $FeGa_{3-x}Ge_x$; x = 0 and x = 0.127 at two temperatures. Inset: temperature dependence of ESR linewidth ΔB.

temperature due to the evolution of strong ferromagnetic correlations, close to the suggested quantum critical point in $FeGa_{3-x}Ge_x$ (Fig. 2b, inset) [4].

Outlook

Band structure calculations show that $T^{(6)}Tr_3$ compounds (T = Cr, Mo, W; Tr = Ga, In) with the $FeGa_3$ crystal structure type are semiconductors. Further calculations assisted by first principles and Boltzmann transport equation suggest high thermopower [2]. Thus, a systematic study on the thermoelectric properties of these compounds and substitution derivatives is being performed.

External Cooperation Partners

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References

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