# Supporting Information

# On Fe–Fe Dumbbells in the Ideal and Real Structure of $FeGa_3$

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Content:

- Results of quantum-chemical calculations.
- Crystallographic data and details of crystal structure refinements.
- **Electron spin resonance (ESR) spectra and remarks.**

Table S1. Decomposition of ELI-D topological features for $FeGa_3$ (attractor) at midpoint $r_c$ of Fe–Fe internuclear line along $z$(i); $\widetilde{\Upsilon}_D^{\alpha}(\boldsymbol{r_c}) = \mathbf{1.01}$; $\boldsymbol{\rho_{\alpha}(r_c)} = \mathbf{0.0193}$; $\widetilde{V}_D^{\alpha}(\boldsymbol{r_c}) = \mathbf{52.3}$.

| Spin a | $\frac{\rho''}{\rho}$ + | $\frac{\tilde{V}_D''}{\tilde{V}_D}$ + | $2\frac{\rho'}{\rho}\frac{\tilde{V}_D'}{\tilde{V}_D}$ | = $\frac{\tilde{\Upsilon}_D''}{\tilde{\Upsilon}_D}$ |
|---|---|---|---|---|
| *z*(i) | +1.20 | –2.96 | 0 | –1.76 |
| *x* | –0.23 | +0.12 | 0 | –0.11 |
| *y* | –0.15 | +0.02 | 0 | –0.13 |
| *type* | (3, –1) | (3, +1) | --- | (3, –3) |
| Sum | +0.82 | –2.82 | 0 | –2.00 |

Table S2. Decomposition of ELI-D topological features for $Fe_2(CO)_9$ (saddle point) at midpoint $r_c$ of Fe–Fe internuclear line along $z$(i); $\widetilde{\Upsilon}_D^{\alpha}(\boldsymbol{r_c}) = \mathbf{0.83}$; $\boldsymbol{\rho_{\alpha}(r_c)} = \mathbf{0.0238}$; $\widetilde{V}_D^{\alpha}(\boldsymbol{r_c}) = \mathbf{35.0}$.

| Spin a | $\frac{\rho''}{\rho}$ + | $\frac{\tilde{V}_D''}{\tilde{V}_D}$ + | $2\frac{\rho'}{\rho}\frac{\tilde{V}_D'}{\tilde{V}_D}$ | = $\frac{\tilde{\Upsilon}_D''}{\tilde{\Upsilon}_D}$ |
|---|---|---|---|---|
| *z*(i) | +2.35 | –3.38 | 0 | –1.03 |
| *x* | +0.10 | –0.05 | 0 | +0.05 |
| *y* | +0.10 | –0.05 | 0 | +0.05 |
| *type* | (3, +3) | (3, –3) | --- | (3, +1) |
| Sum | +2.55 | –3.48 | 0 | –0.93 |

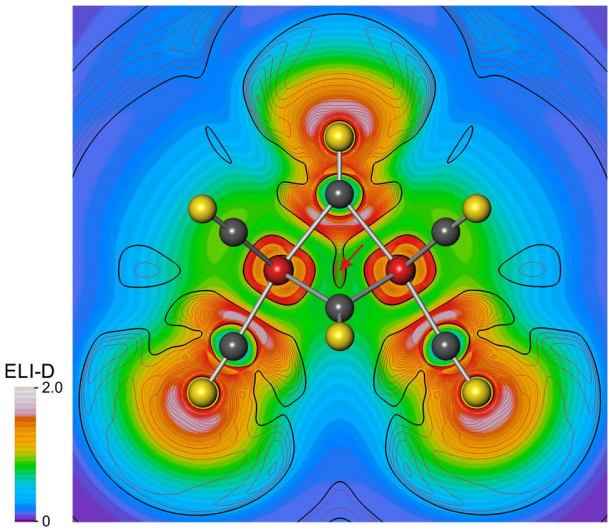


Figure S1. ELI-D slice for $Fe_2(CO)_9$ using indicated color-map; isolines of the relative ELI-D Laplacian in the range $-2 \le \nabla^2\widetilde{\Upsilon}_D^{\alpha}/\widetilde{\Upsilon}_D^{\alpha} \le -0.2$ are shown in red, isoline of $\nabla^2\widetilde{\Upsilon}_D^{\alpha}/\widetilde{\Upsilon}_D^{\alpha} = 0$ is shown in black; Fe–Fe bond midpoint with negative ELI-D Laplacian is indicated by a red arrow; Fe, C, and O atoms are shown as red, grey, and yellow spheres, respectively.

Table S3. Crystallographic data and refinement of the ideal crystal structure of $FeGa_3$ (crystal 1)

| | |
|---|---|
| Molar mass | 265.01 |
| Crystal color, shape | Gray, prismatic |
| Crystal dimensions ($mm^3$) | 0.100 × 0.100 × 0.080 |
| Space group, $Z$ | $P4_2/mnm$ (no. 136), 4 |
| Lattice parameters (pm) | $a$ = 626.53(1) |
| (from powder data) | $c$ = 655.85(2) |
| $V$ ($10^6$ $pm^3$), $\rho$ (g $cm^{-3}$) | 257.45(2), 6.84 |
| Diffractometer, detector | Rigaku AFC7, CCD Saturn724+ |
| Radiation | Mo $K\alpha$ ($\lambda$ = 71.073 pm) |
| Exposures, steps (degree) | 720, $\varphi$ = 0.5 |
| Absorption correction | Multi-scan ($\mu$ = 379.8 $cm^{-1}$) |
| $T_{min}/T_{max}$ | 0.681 / 1.000 |
| $2\theta_{max}$ | 80.5° |
| $hkl$ range | $-11 < h < 8$ |
| | $-11 < k < 7$ |
| | $-11 < l < 11$ |
| Measured/unique reflections | 3059 / 466 |
| $R$(int) | 0.029 |
| Observation criteria | $F(hkl) > 4\sigma F(hkl)$ |
| Refinement | Full-matrix least-squares on $F^2$ (16 parameters) |
| $R(F)$, $Rw$, goodness-of-fit | 0.033, 0.036, 1.194 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ (e $Å^{-3}$) | -1.84, 2.95 |

Table S4. Atomic position and anisotropic displacement parameters for $FeGa_3$.

| Atom | Fe | Ga1 | Ga2 |
|---|---|---|---|
| Site | 4*f* | 4*c* | 8*j* |
| *x*/*a* | 0.15639(8) | 0 | 0.84433(5) |
| *y*/*b* | *x* | ½ | -*x* |
| *z*/*c* | 0 | 0 | 0.23790(7) |
| s.o.f. | 1.0 | 1.0 | 1.0 |
| $U_{11}$ | 54(2) | 124(3) | 91(2) |
| $U_{22}$ | $U_{11}$ | 60(2) | $U_{11}$ |
| $U_{33}$ | 46(2) | 134(3) | 81(2) |
| $U_{12}$ | -2(2) | 18(2) | 6(1) |
| $U_{13}$ | 0 | 0 | 21(1) |
| $U_{23}$ | 0 | 0 | $-U_{13}$ |
| $U$(iso/eq) | 51(2) | 106(2) | 88(1) |

By considering the strong anisotropy of atomic displacement parameters (ADPs) for the Ga1 position ($U_{11} \approx U_{33} >> U_{22}$, Table S2) a split model for this Ga site was applied, yielding analogous results as described in the crystal structure refinement of $RuGa_3$ [50].

Independently, after the refinement considering the 'Fe2' position a further residual maximum in the difference Fourier (coordinates *x y z* = 0 ½ 0.048) was found, close to Ga1. This additional maximum was considered in the refinement and was assigned as 'Ga3'. Both Ga1 and 'Ga3' were isotropically refined, fixing $U_{11}$ for 'Ga3' equal to $U_{eq}$ of Ga2 (90 $pm^2$). The site occupation factor was restrained as the complement for the Ga1 position (Ga1(s.o.f.) + 'Ga3'(s.o.f.) = 1) and with the constrain that 'Fe2'(s.o.f.) = 'Ga3'(s.o.f.). The resulting residual value is higher but still within a satisfactory range ($R1$ = 0.045) taking into account that some atomic positions were isotropically refined. The crystal structure refinement shows the additional 'Ga3' site splitting parallel to [001] is in direct connection with the presence of 'Fe2' in the neighboring trigonal prism (Ga1–'Fe2' = 237 pm).

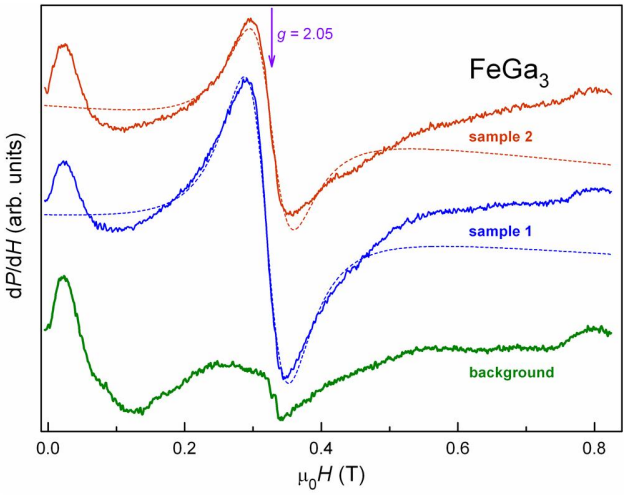


Figure S2. ESR spectra of two $FeGa_3$ samples and paraffin filled suprasil tube (background).

Figure S2 shows ESR spectra (first derivative of absorbed microwave power, d*P*/d*H*, vs. external magnetic field *H*) of $FeGa_3$ and a paraffin filled suprasil tube („background") taken at a microwave frequency of 9.4 GHz and a temperature of 295 K. The two ESR samples of $FeGa_3$ have comparable masses (11.1 mg and 11.2 mg) and originate from the two batches discussed in this paper, „sample 1" and „sample 2", respectively. The spectra amplitudes of $FeGa_3$ are normalized to the resonator quality factor which moderately differs for the two samples. Note the considerable background contribution to the $FeGa_3$ spectra. The dashed lines denote Lorentzian line shapes at a resonance field corresponding to an effective *g*-value of *g* = 2.05. This demonstrates the existence of ESR active centers in the two $FeGa_3$ samples. The intensities of the two Lorentzian lines have a ratio of 2.6, i.e. the concentration of ESR-active centers in sample 1 is considerably higher than in sample 2.

The temperature dependencies of the $FeGa_3$ ESR parameters are well in agreement with those reported previously[10].

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