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Supplemental material information. *Calibration of ^{57}Fe Mössbauer constants by first principles.*.

Silvia Casassa,*[a] and Anna Maria Ferrari[a]

	Q_{net}			Volume		
	PBE	PBE0	HF	PBE	PBE0	HF
FeF_2	1.54	1.63	1.77	66.9	65.1	64.4
$FeCl_2$	1.21	1.34	1.55	74.2	71.0	65.1
$FeBr_2$	1.06	1.22	1.47	85.5	81.1	73.4
FeI_2	0.76	0.96	1.29	96.1	89.8	79.2
FeO	1.34	1.44	1.62	62.4	60.3	56.1
FeF_3	2.03	2.23	2.57	49.4	47.0	42.9
$FeCl_3$	1.42	1.65	2.18	65.7	61.8	53.3
Fe_2O_3	1.58	1.96	2.37	56.4	50.8	45.1
FeAl	-1.26	-1.45	-1.90	110.6	115.1	127.8
Fe	0.00	0.00	0.0	76.3	76.3	76.4
FeTi	-0.83	-1.04	-1.33	100.1	103.1	107.3

Table S.I Net charges, Q_{net}, and volume, in a.u., refer to ^{57}Fe in different crystalline compounds, as evaluated by Bader topological analysis of the electron density. For sake of comparison, the primitive cell of Iron is 76.6 a.u..

	$\rho_e^A - \rho_e^S$ (a.u.)								$\delta(mm/s)$
	PBE	PWGGA	M06L	B3LYP	PBE0	M06	M062X	HF	exp
FeF_2	-3.514	-3.506	-3.528	-3.614	-3.761	-3.445	-3.874	-5.474	1.467[1,2]
$FeCl_2$	-2.847	-2.836	-2.938	-2.951	-3.074	-2.756	-3.280	-4.809	1.30[2,3]
$FeBr_2$	-2.801	-2.787	-2.945	-2.839	-2.988	-2.643	-3.202	-4.745	1.120[4]
FeO	-2.794	-2.794	-2.712	-2.789	-2.832	-2.516	-3.235	-4.515	1.15[5]
FeI_2	-2.646	-2.639	-2.672	-2.684	-2.844	-2.412	-3.121	-4.542	1.044[4]
FeF_3	-1.870	-1.866	-1.632	-1.602	-1.623	-1.419	-1.605	-2.666	0.489[6]
$FeCl_3$	-1.728	-1.727	-1.595	-1.415	-1.381	-1.085	-1.284	-1.942	0.45[7]
Fe_2O_3	-1.592	-1.603	-1.285	-1.157	-1.150	-0.912	-1.149	-2.027	0.37[8]
AlFe	-1.077	-1.074	-0.992	-0.825	-0.882	-1.156	-0.571	-0.698	0.25[9]
TiFe	0.503	0.507	0.554	0.729	0.929	0.288	1.040	0.177	-0.145[10]

Table S.II Absolute values of the electron density on ^{57}Fe, $\rho^A(\mathbf{r})$, for compounds in the calibration set, can be inferred referring to the value of $\rho^S(\mathbf{r}) \equiv \rho^{Fe}(\mathbf{r})$ reported in Table II of the manuscript.

	V_{ZZ} $(10^{21} V/m^2)$					$\Delta E_Q(mm/s)$
	PBE	CP(PPP)/PBE	PWGGA	M06L	**Exp**	Exp
FeF_2	17.37	17.72	17.54	16.62	17.1[11]	2.85[6]
$FeCl_2$	1.50	1.86	1.86	2.05	6.01[12]	1.210[4]
$FeBr_2$	0.89	0.99	0.85	1.09	6.61[13]	1.132[4]
FeI_2	0.63	0.87	0.65	1.62	0.1	0.962[4]
Fe_2O_3	1.64	1.75	2.04	1.51	2.16[14]	0.12[15]
$FeCl_3$	-0.38	-0.34	-0.36	-0.30		0.04[4]
FeF_3	0.34	0.44	0.32	0.58		0.044[6]

Table S.III V_{ZZ} component of the electric field gradient at the ^{57}Fe nucleus. CP(PPP) basis set by Neese and coworkers.[16] Experimental EFG and quadrupolar splittings are reported in the sixth and last column, respectively.[17]

[a] *Dipartimento di Chimica and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces), Università degli Studi di Torino, via P. Giuria 5, I-10125 Torino, Italy. E-mail: silvia.casassa@unito.it*

References

1 M. Filatov, *J. Chem. Phys.*, 2007, **127**, 084101.
2 L. Walker, G. Wertheim and V. Jaccarino, *Phys. Rev. Lett.*, 1961, **6**, 98.
3 R. Axtmann, Y. Hazony and J. H. Jr., *Chem. Phys. Lett.*, 1968, **2**, 673.
4 E. Pfletschinger and D. Buchanan, *Z. Phys.*, 1968, **209**, 119.
5 G. Shirane, D. E. Cox and S. Ruby, *Phys. Rev.*, 1962, **4**, 1158.
6 G. Wertheim, H. Guggenheim and D. Buchanan, *Phys. Rev.*, 1968, **169**, 465.
7 S. DeBenedetti, G. Lang and R. Ingalls, *Phys. Rev. Lett.*, 1961, **6**, 60.
8 M. Dyar, D. Agresti, M. Schaefer, C. Grant and E. Sklute, *Ann. Rev. Earth Planet Sci.*, 2006, **34**, 83.
9 C. Jeandey and P. Peretto, *J. Physique*, 1975, **36**, 1103.
10 E. Mielczarek and W. Winfree, *Phys. Rev. B*, 1975, **11**, 1026.
11 G. Wertheim and D. Buchanan, *Phys. Rev.*, 1967, **161**, 478.
12 D. Simkin, *Phys. Rev.*, 1969, **177**, 1008.
13 G. Bancroft and J. Dubery, *J. Chem. Phys.*, 1969, **50**, 2264.
14 R. Vaughan and H. Drickamer, *J. Chem. Phys.*, 1967, **47**, 1530.
15 O. Kistner and A. Sunyar, *Phys. Rev. Lett.*, 1960, **4**, 412.
16 M. Römelt, S. Ye and F. Neese, *Inor. Chem.*, 2009, **48**, 784–785.
17 H. Fjellvag, B. C. Hauback, T. Vogt and S. Stolen, *American Mineralogist*, 2002, **87**, 347–349.

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