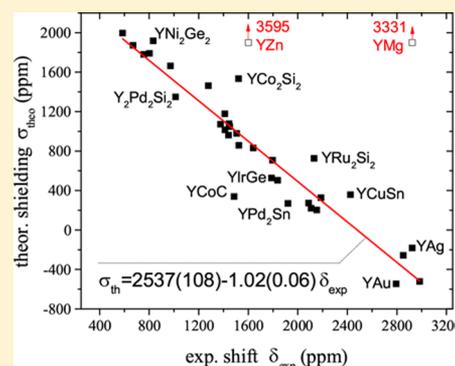


# Computational Study of Y NMR Shielding in Intermetallic Yttrium Compounds

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**ABSTRACT:** Density functional theory (DFT) calculations of the magnetic shielding for solid state nuclear magnetic resonance (NMR) provide an important contribution for the understanding of experimentally observed signals. In this work, we present calculations of the Y NMR shielding in intermetallic compounds (YMg, YT, YTX, YT<sub>2</sub>X, YT<sub>2</sub>X<sub>2</sub>, Y<sub>2</sub>TB<sub>6</sub>, and Y<sub>2</sub>TSi<sub>3</sub> where T represents various transition metals and X refers to group IV elements C, Si, Ge, Sn, Pb). The total shielding  $\sigma$  of this selection varies by about 2500 ppm and correlates very well with the experimentally observed shifts except for YMg and YZn. These two simple compounds have a spike in the DOS at  $E_F$  and a corresponding huge spin susceptibility which leads to the disagreement. It could be a problem of DFT (neglect of spin fluctuations), but we would interpret the discrepancies as caused by disorder which could be present in the experimental samples because disorder removes the spike in the DOS. The diamagnetic contribution  $\sigma_o$  (chemical shift) is by no means constant as often assumed when interpreting experimental metallic shifts and varies up to 1500 ppm, but still the dominating term is the spin contact term  $\sigma_c$ . Although all compounds are metals, only half of them have a paramagnetic (negative)  $\sigma_c$  due to the reoccupation of the valence Y-*s*s electrons, while for others the large induced Y-*d* magnetic moment induces a diamagnetic core polarization. In most of our cases, the spin dipolar contribution  $\sigma_{sd}$  is fairly small with  $|\sigma_{sd}|$  less than 100 ppm and often even much smaller except in a few very asymmetric compounds like YCo<sub>2</sub>Si<sub>2</sub> and YRu<sub>2</sub>Si<sub>2</sub> ( $\sigma_{sd} \approx 320$  ppm).



## INTRODUCTION

Ab initio calculation of NMR shielding for insulating solids is nowadays relatively easy and quite common;<sup>1,2</sup> however, such calculations are much more complicated for metallic systems, and only very few studies have been published so far.<sup>3–6</sup> The complications arise mainly from two facts, namely, numerical problems for an exact description of the Fermi surface (i.e., the eigenstates have to be determined on a very dense *k*-mesh, and even then results may vary with the applied temperature broadening) and the limited accuracy of present density functionals because for NMR shifts of metals not only the average electronic structure must be reasonably well described but also in particular the states at the Fermi energy ( $\epsilon_F$ ) need to be known very accurately. In fact, the well-known overestimation of magnetism in a few cases with our present approximate density functionals, in particular the generalized gradient approximation (GGA), can cause severe problems as it may lead to a ferromagnetic ground state instead of a nonmagnetic state.<sup>7–9</sup>

A traditional view of Knight shifts is that only the valence *s*-electrons at the Fermi energy determine the shielding, and the “constant” diamagnetic orbital part is unimportant. Thus, one often tries to correlate the *s*-partial density of states (PDOS) at  $\epsilon_F$  with the measured shielding. However, even with the limited experience we have so far, it turns out that this is only true for very simple alkali or alkali-earth metals but not for more

complicated elements. For instance, for transition metals the total spin contact term is not at all proportional to the *s*-PDOS since an induced *d* magnetic moment may polarize core electrons in the opposite way and dominate the shielding.<sup>3</sup> On the other hand in metallic gallides<sup>4</sup> the orbital contribution is not a constant, and in particular in BaGa<sub>2</sub> the spin-dipolar contribution is a major contribution and not just a small correction.

In this work we compute the spin and orbital components of the isotropic shielding for Y in various intermetallic yttrium compounds covering a wide range of atomic and electronic structures. We unravel the relation between the spin component of the shielding and the Y-*s* and Y-*d* PDOS at  $\epsilon_F$  and the correlation between the core and semicore contribution to the spin contact term with the induced Y magnetic moment. In addition we show the importance of the orbital contribution, which is by no means a “constant” for different Y-compounds.

## THEORY AND COMPUTATIONAL DETAILS

Nuclear magnetic resonance (NMR) spectroscopy measures the response of a material to an external magnetic field by detecting the transition energy related to the reorientation of

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the nuclear magnetic moment. The NMR shielding tensor  $\sigma$  is defined as a proportionality constant between the induced magnetic field  $B_{\text{ind}}$  at the nucleus at the site  $R$  and the external uniform field  $B$ :

$$\vec{B}_{\text{ind}}(R) = -\vec{\sigma}(R)\vec{B} \quad (1)$$

Often only the isotropic shielding can be accessed experimentally which is given by the trace of the shielding tensor  $\sigma(\mathbf{R}) = \text{Tr}[\vec{\sigma}(\mathbf{R})]$ . The experimentally measured isotropic chemical shift  $\delta$  and the absolute isotropic shielding  $\sigma$  are related through a reference compound and defined by  $\delta(\mathbf{R}) = \sigma_{\text{ref}} - \sigma(\mathbf{R})$ .

In metals we identify three distinct contributions to the induced field: an orbital ( $\vec{B}_o$ ), a spin-dipolar ( $\vec{B}_{\text{sd}}$ ), and an isotropic spin contact contribution ( $\vec{B}_c$ ).

$$\vec{B}_{\text{ind}} = \vec{B}_o + \vec{B}_c + \vec{B}_{\text{sd}} \quad (2)$$

For the orbital component the external magnetic field modifies the orbital motion, and as a result an induced current appears. The corresponding induced orbital magnetic field  $B_o$  can be obtained directly from Biot–Savart's law (in atomic units, with  $c$  as speed of light)

$$B_o(\mathbf{R}) = \frac{1}{c} \int d^3j_{\text{ind}}^{\text{orb}} \times \frac{\mathbf{R} - \mathbf{r}}{|\mathbf{r} - \mathbf{R}|^3} \quad (3)$$

where  $j_{\text{ind}}$  is the induced orbital current calculated within a linear response approach<sup>1,10,11</sup> originally developed by Mauri, Pfommer, and Louie (MPL).<sup>10</sup> The approach has been adapted and implemented within the all-electron, full potential augmented plane wave (APW) WIEN2k code.<sup>12,13</sup>

In order to compute the induced spin density and the corresponding contact  $B_c$  and spin dipolar  $B_{\text{sd}}$  components of the induced field we apply a direct approach<sup>3</sup> and perform self-consistent spin-polarized calculations with a finite external magnetic field ( $B_{\text{ext}}$ ) acting only on the electronic spin. The interaction with  $B_{\text{ext}}$  can be cast into a spin-dependent potential leading to a shift of the effective exchange-correlation potential for the two spins and causing a finite spin magnetization. It does not break the symmetry of the solid, and therefore such calculations are straightforward. The method is an alternative to the linear response formalism proposed by F. Mauri.<sup>14</sup> Our recent findings indicate that in many cases a considerable portion of the response can be computed only in a self-consistent way, for instance, the contributions from the polarization of the core and semicore states.

$B_c$  and  $B_{\text{sd}}$  are computed using the classic expression for the magnetic hyperfine field<sup>15</sup> consisting of two terms, the Fermi contact term  $B_c$  and the spin-dipolar contribution  $B_{\text{sd}}$

$$B_{\text{hf}} = \frac{8\pi}{3} m_{\text{av}} + \int \frac{S(\mathbf{r})}{r^3} [3(m(\mathbf{r})\hat{r})\hat{r} - m(r)] \quad (4)$$

where the first term corresponds to  $B_c$  and the second captures  $B_{\text{sd}}$ . The corresponding spin contribution ( $\sigma_s$ ) to the shielding is then simply given by

$$\sigma_s = \sigma_c + \sigma_{\text{sd}} = -B_c/B_{\text{ext}} - B_{\text{sd}}/B_{\text{ext}} \quad (5)$$

The Fermi contact shielding  $\sigma_c$  is calculated in a region near the nucleus with a diameter equal to the Thomson radius. It is proportional to the average spin density ( $m_{\text{av}}(r) = \rho_{\text{up}}(r) - \rho_{\text{down}}(r)$ ) in this region. The value of the spin-dipolar component ( $\sigma_{\text{sd}}$ ) comes almost entirely from within the atomic sphere, therefore it can be expressed in terms of elements of the

density matrix.<sup>3</sup> In order to induce a sizable spin density we apply an external field  $B_{\text{ext}}$  of 100 T. We have also checked the linearity of the induced magnetic field with respect to the external magnetic field for several compounds, in particular also for the problematic YMg and YZn compounds, which have a much too large spin contribution. In the APW method, the unit cell is decomposed into nonoverlapping atomic spheres and an interstitial region. The unperturbed wave functions as well as their first-order perturbations are expressed using plane waves augmented with an atomic like angular momentum expansion inside the atomic spheres  $S_\alpha$ .

$$\psi_{n,k(\mathbf{r})} = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_G C_G^{n,k} e^{i(G+k)r}, & r \in I \\ \sum_{lm} W_{lm}^{n,\alpha,k}(\mathbf{r}) Y_{lm}(\hat{r}), & r \in S_\alpha \end{cases} \quad (6)$$

Inside the atomic spheres APW uses numerical radial functions  $W_{lm}^{n,\alpha,k}(r)$  computed at predefined linearization energies,<sup>13</sup> which are chosen to match the energies of the corresponding occupied bands. This approach yields basically the exact radial wave function for the occupied and shallow conduction band states. However, it is not a complete basis and not well suited to expand the perturbation of the wave function due to an external magnetic field as needed for the orbital component. This issue can be solved by adding additional local orbitals at high energies to the basis. Specifically we supply eight additional local orbitals (NMR-LOs) for orbital numbers  $l \leq 3$ . The radial wave functions for those NMR-LOs are evaluated at higher energies<sup>2</sup> selected such that an additional radial node is introduced for each subsequent NMR-LO. Besides this, the perturbed wave functions are augmented with radial functions proportional to  $r \frac{\partial}{\partial r} u(r)$ .<sup>16</sup> This makes the method basically numerically exact within a given density functional theory (DFT) approximation.<sup>16,17</sup>

In metallic systems the presence of a Fermi surface considerably impedes the convergence of the calculated shielding with respect to the density of the Brillouin zone (BZ) sampling. Usually, a Fermi smearing of the occupancy around  $\epsilon_F$  makes the process easier. In this work, all quoted results are computed with a Fermi smearing of  $k_B T = 4$  mRy, and in addition, we specify the dependency with respect to the smearing parameter  $k_B T$  by quoting the factor  $d\sigma/d(k_B T)$ , where  $\sigma$  stands for the corresponding shielding component. For most of the cases we were able to reach convergence below 1 ppm for k-meshes of  $k_1 = 10^6$ ,  $k_2 = 50\,000$ , and  $k_3 = 10\,000$  k-points in the full BZ. Only for a few cases, where perfect convergence has not been reached, we estimate the uncertainty related to the k-point convergence by quoting the change of shielding when reducing the k-mesh by a factor of 2 (for  $k_1$  and  $k_3$ ) or 5 (for  $k_2$ ). Other computational parameters like angular momentum expansions of charge densities, potentials, and wave functions inside the atomic spheres as well as the linearization energies are kept as set by WIEN2k defaults. The plane wave basis set size was determined using  $RK_{\text{max}} = 8$  (except for the hexaborides with their small B-sphere, where  $RK_{\text{max}} = 7$  is sufficient), and we keep the atomic sphere radii for Y atoms constant at 2.3 au. In all cases, the Perdew, Burke, Ernzerhof (PBE)<sup>18</sup> version of the GGA is used for the DFT exchange-correlation functional.

## RESULTS AND DISCUSSION

For the selection of compounds considered in this work we follow refs 19–22. The space group and lattice parameters for the whole set are provided in Table 1. Since the specific coordination of the Y atoms determines the NMR shifts, we start with the brief description of the structural details of our compounds.

**Table 1. Space Group and Lattice Parameter [Å] of Yttrium Compounds (Compounds Denoted by \* Have Two Different Y Sites)<sup>a</sup>**

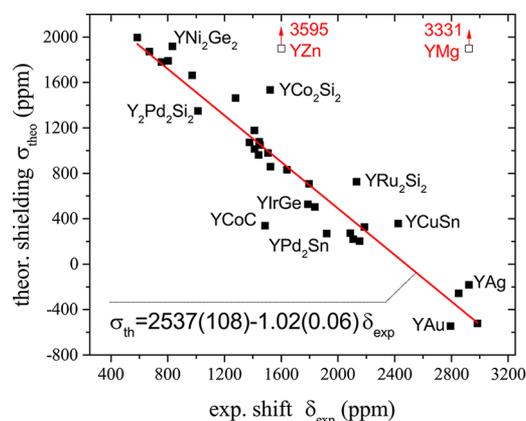
compound	space group	a	b	c	ref
YMg	<i>Pm</i> $\bar{3}$ <i>m</i>	3.793	a	a	25
YCu	<i>Pm</i> $\bar{3}$ <i>m</i>	3.476	a	a	26
YZn	<i>Pm</i> $\bar{3}$ <i>m</i>	3.578	a	a	27
YAg	<i>Pm</i> $\bar{3}$ <i>m</i>	3.640	a	a	28
YAu	<i>Pm</i> $\bar{3}$ <i>m</i>	3.583	a	a	29
YNi <sub>2</sub> Si <sub>2</sub>	<i>I4</i> / <i>mmm</i>	3.955	a	9.568	19
YNi <sub>2</sub> Ge <sub>2</sub>	<i>I4</i> / <i>mmm</i>	4.035	a	9.757	30
YCo <sub>2</sub> Si <sub>2</sub>	<i>I4</i> / <i>mmm</i>	3.888	a	9.734	19
YCu <sub>2</sub> Si <sub>2</sub>	<i>I4</i> / <i>mmm</i>	3.971	a	9.981	31
YRu <sub>2</sub> Si <sub>2</sub>	<i>I4</i> / <i>mmm</i>	4.158	a	9.546	19
YRh <sub>2</sub> Si <sub>2</sub>	<i>I4</i> / <i>mmm</i>	4.018	a	9.897	19
YPd <sub>2</sub> Si <sub>2</sub>	<i>I4</i> / <i>mmm</i>	4.128	a	9.857	19
YAgSi	<i>P</i> $\bar{6}$ 2 <i>m</i>	7.024	a	4.170	32
YRhSn	<i>P</i> $\bar{6}$ 2 <i>m</i>	7.540	a	3.770	33
YCuSn	<i>P</i> 6 <sub>3</sub> <i>mc</i>	4.513	a	7.274	34
YCuPb	<i>P</i> 6 <sub>3</sub> <i>mc</i>	4.559	a	7.334	35
YAgSn	<i>P</i> 6 <sub>3</sub> <i>mc</i>	4.683	a	7.372	23
YPd <sub>2</sub> Sn	<i>Fm</i> $\bar{3}$ <i>m</i>	6.714	a	a	20
YNiSi	<i>Pnma</i>	6.870	4.155	7.205	36
YNiGe	<i>Pnma</i>	6.900	4.203	7.287	21
YNiSn	<i>Pnma</i>	7.135	4.448	7.675	37
YNiPb	<i>Pnma</i>	7.150	4.513	7.752	21
YPdSn	<i>Pnma</i>	7.154	4.588	7.891	20
YIrSi	<i>Pnma</i>	6.788	4.183	7.464	21
YIrGe	<i>Pnma</i>	6.834	4.263	7.619	21
YIrSn	<i>Pnma</i>	6.936	4.516	7.968	21
Y <sub>2</sub> RhSi <sub>3</sub> *	<i>P</i> 6 <sub>3</sub> / <i>m</i> <i>mc</i>	8.126	a	7.872	22
YRh <sub>2</sub> Si*	<i>P</i> 6 <sub>3</sub> / <i>m</i> <i>mc</i>	5.495	a	15.030	38
Y <sub>2</sub> ReB <sub>6</sub> *	<i>Pb</i> <i>am</i>	9.175	11.551	3.673	38
Y <sub>2</sub> RuB <sub>6</sub> *	<i>Pb</i> <i>am</i>	9.163	11.503	3.644	22
YCoC	<i>P</i> 4 <sub>2</sub> / <i>m</i> <i>mc</i>	3.650	a	6.864	24

<sup>a</sup>Free internal coordinates have been optimized theoretically.

YT compounds with T = Au, Cu, Zn, Ag, and YMg have CsCl structure, a primitive cubic lattice with two atoms per unit cell, where both atoms have 8-fold coordination. The YT<sub>2</sub>Si<sub>2</sub> and YT<sub>2</sub>Ge<sub>2</sub> silicides/germanides (T = Ni, Cu, Pd, Ru, Rh, and Co) have the ThCr<sub>2</sub>Si<sub>2</sub> structure type. The transition metal atoms have tetrahedral Si/Ge coordination with T–Si distances close to the sum of the covalent radii. Layers of edge-sharing TS<sub>4</sub>/4 tetrahedra are connected via Si–Si bonding. The three-dimensional [T<sub>2</sub>Si<sub>2</sub>] polyanionic network leaves larger cages which are filled by the Y atoms, and each yttrium atom has eight Si or Ge nearest neighbors (NN) which form a planar square net above and below Y.<sup>19</sup> YAgSi and YRhSn have a hexagonal structure (space group *P*62*m*). Their structure consists of Y–Si(Rh) and Ag(Rh)–Si(Sn) hexagonal planes which alternate along the *c*-axis. Each yttrium has 5 Si(Rh) first NN, where one is in-plane and 4 are out-of-plane neighbors.

The nearest Y–Y distances (4 in-plane and 2 out-of-plane) vary a lot in the two compounds.<sup>23</sup> YCuSn, YCuPb, and YAgSn also have a hexagonal structure, where the hexagonal Y-layers are sandwiched by buckled CuSn, CuPb, and AgSn hexagons, respectively. In the cubic Heusler compound YPd<sub>2</sub>Sn (MnCu<sub>2</sub>Al structure type) each Y atom has octahedral Sn coordination and additionally eight Pd neighbors. The Y atoms have cubic site symmetry, and the shortest Y–Y distance is much larger than in hcp yttrium.<sup>20</sup> The equiatomic Y compounds YTX (T = Ni, Ir, Pd and X = Si, Ge, Sn, Pb) crystallize with orthorhombic TiNiSi-type structure, having space group *Pnma* and four formula units per cell. Each Y atom is coordinated by two ordered but strongly puckered T<sub>3</sub>X<sub>3</sub> hexagons, showing a strong tilt and formation of interlayer T–X bonds. In the case of YIrSi/Ge the Y atoms have five Si/Ge NN, while there are mixed T and Si/Ge NN in the other compounds.<sup>21</sup> Y<sub>2</sub>RhSi<sub>3</sub> is an ordered hexagonal superstructure, where the Rh and Si atoms form slightly puckered [RhSi<sub>3</sub>]<sup>δ-</sup> polyanionic networks in a honeycomb arrangement. The Y atoms form distorted hexagonal planes, where the coloring within the [RhSi<sub>3</sub>] polyanionic network leads to different coordinations for Y1 (Wyckoff site 6h, with 4 Rh, and 8 Si neighbors) and Y2 (Wyckoff site 2b, 12 Si neighbors), both with distorted hexagonal prismatic coordination. The hexagonal structure of YRh<sub>2</sub>Si is an ordered CeNi<sub>3</sub> derivative. The coordination of the two crystallographically independent Y is Wyckoff site 2c (6 in-plane NN Si atoms) and 4f (3 + 6 Rh NN).<sup>22</sup> In Y<sub>2</sub>ReB<sub>6</sub> and Y<sub>2</sub>RuB<sub>6</sub> six crystallographically independent B atoms build up planar networks that can be considered as a tessellation of slightly distorted pentagons, hexagons, and heptagons. These networks show AA stacking, and the pentagonal, hexagonal and heptagonal prismatic voids are filled by Ru(Re), Y1, and Y2 atoms. The two distinct Y sites in 4h Wyckoff positions have 14 or 12 B NN and also differ in their in-plane neighbors.<sup>22</sup> We also consider YCoC (space group *P*4<sub>2</sub>/*m**mc*) where Y and Co atoms are arranged in a distorted CsCl structure, and C atoms reside in 1/3 of the octahedral voids with 4 Y and 2 Co neighbors.<sup>24</sup>

Figure 1 and Table 2 compare the calculated shielding and the measured isotropic shifts.<sup>19,21,22</sup> The theoretical values correlate very well with the experimentally observed shift, using a linear regression. The constant coefficient (reference) is equal



**Figure 1.** Comparison of the calculated theoretical shielding ( $\sigma_{\text{theo}}$ ) with the measured shifts  $\delta_{\text{exp}}$  (ppm). The least-squares fit has been obtained without YMg and YZn. Only compounds with larger deviations from the linear fit are labeled.

**Table 2.** Theoretical NMR Isotropic Shielding  $\sigma_{\text{theo}}$  and the Decomposition into Orbital ( $\sigma_o$ ), Spin Contact ( $\sigma_c$ ), and Spin Dipolar ( $\sigma_{\text{sd}}$ ) Terms Calculated with a Fermi Smearing of 4 mRy and with the Number of k-Points in the Full BZ as Indicated by the Labels  $k_1 = 10^6$ ,  $k_2 = 50\,000$ , and  $k_3 = 10\,000^a$

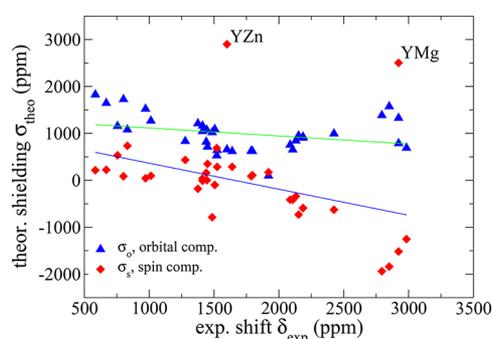
compound	site	$\sigma_o$	$\sigma_c$	$\sigma_{\text{sd}}$	$\sigma_{\text{theo}}$	$\delta_{\text{exp}}$	$\delta_{\text{theo}}$
YCu <sup>k<sub>1</sub></sup>		1574 (0,0)	-1838 (0,-48)	7 (0,0)	-257	2851	2730
YAg <sup>k<sub>1</sub></sup>		1328 (0,-6)	-1517 (-1,51)	7 (0,0)	-182	2923	2657
YAu <sup>k<sub>1</sub></sup>		1385 (0,8)	-1937 (5,52)	6 (0,0)	-546	2794	3012
YNi <sub>2</sub> Si <sup>k<sub>2</sub></sup>		1155 (0,-4)	533 (4,0)	92 (0,2)	1780	756	739
YNi <sub>2</sub> Ge <sup>k<sub>2</sub></sup>		1080 (0,4)	735 (2,2)	103 (0,0)	1918	832	605
YCo <sub>2</sub> Si <sup>k<sub>2</sub></sup>		528 (0,5)	686 (0,-36)	321 (0,-12)	1535	1521	979
YCu <sub>2</sub> Si <sup>k<sub>2</sub></sup>		1826 (2,0)	215 (0,0)	-45 (0,-2)	1996	585	528
YRu <sub>2</sub> Si <sup>k<sub>2</sub></sup>		845 (0,-19)	-341 (0,-1)	222 (0,-1)	726	2131	1769
YRh <sub>2</sub> Si <sup>k<sub>2</sub></sup>		834 (0, 3)	434 (0,10)	196 (0,2)	1464	1278	1048
YPd <sub>2</sub> Si <sup>k<sub>2</sub></sup>		1269 (0,-1)	96 (-25,-5)	-15 (0,-1)	1350	1013	1160
YAgSi <sup>k<sub>2</sub></sup>		1072 (0,0)	3 (0,8)	2 (0,0)	1077	1445	1426
YRhSn <sup>k<sub>2</sub></sup>		755 (0,0)	-413 (5,-44)	-69 (2,24)	273	2087	2212
YCuSn <sup>k<sub>2</sub></sup>		995 (-1,0)	-626 (10,14)	-11 (0,-6)	358	2425	2129
YCuPb <sup>k<sub>1</sub></sup>		930 (0,-2)	-589 (0,-22)	-14 (0,2)	327	2186	2159
YAgSn <sup>k<sub>2</sub></sup>		951 (0,-2)	-731 (-8,-21)	-16 (0,0)	204	2152	2279
YPd <sub>2</sub> Sn <sup>k<sub>2</sub></sup>		97 (0,-1)	171 (0,7)	2 (0,0)	270	1920	2215
YNiSi <sup>k<sub>2</sub></sup>		642 (0,-6)	286 (0,-6)	-70 (0,8)	916	1524	1640
YNiGe <sup>k<sub>2</sub></sup>		713 (0,-2)	351 (-1,10)	-15 (0,0)	1049	1450	1454
YNiSn <sup>k<sub>2</sub></sup>		619 (-9,-4)	287 (0,8)	-75 (0,-5)	831	1640	1667
YNiPb <sup>k<sub>2</sub></sup>		621 (0,-7)	109 (0,-13)	-23 (0,0)	707	1796	1788
YPdSn <sup>k<sub>2</sub></sup>		819 (0,0)	159 (0,11)	-16 (0,0)	962	1440	1539
YIrSi <sup>k<sub>2</sub></sup>		582 (0,0)	125 (1,5)	-203 (0,2)	504	1837	1986
YIrGe <sup>k<sub>2</sub></sup>		626 (0,0)	89 (1,5)	-187 (0,2)	528	1787	1963
YIrSn <sup>k<sub>2</sub></sup>		654 (0,0)	-414 (0,3)	-19 (0,-2)	221	2107	2263
Y <sub>2</sub> RhSi <sub>3</sub> <sup>k<sub>3</sub></sup>	6h	1212 (0,0)	-180 (-1,0)	40 (0,0)	1072	1376	1431
	2b	1646 (0,0)	224 (0,0)	2 (0,0)	1872	669	650
YRh <sub>2</sub> Si <sup>k<sub>3</sub></sup>	2c	1163 (2,-6)	-10 (15,64)	-138 (9,-6)	1002	1412	1487
	4f	690 (0,-6)	-1253 (-67,-10)	42 (3,0)	-557	2984	2988
Y <sub>2</sub> ReB <sub>6</sub> <sup>k<sub>3</sub></sup>	4h <sub>1</sub>	1522 (0,-4)	43 (-1,-1)	98 (0,31)	1663	972	854
	4h <sub>2</sub>	1044 (0,-5)	39 (1,-36)	95 (0,67)	1178	1411	1328
Y <sub>2</sub> RuB <sub>6</sub> <sup>k<sub>3</sub></sup>	4h <sub>1</sub>	1727 (0,0)	86 (-11,-6)	-23 (0,0)	1790	802	730
	4h <sub>2</sub>	1089 (0,2)	-98 (14,-18)	-12 (62,-2)	979	1506	1522
YCoC <sup>k<sub>1</sub></sup>		1022 (0,-15)	-787 (0,-51)	105 (0,-1)	340	1486	2146
YMg <sup>k<sub>1</sub></sup>		788 (0,10)	2502 (4,-303)	41 (0,-5)	3331	2923	-776
YZn <sup>k<sub>1</sub></sup>		657 (0,0)	2900 (-50,-464)	38 (2,6)	3595	1600	-1034

<sup>a</sup>The numbers in parentheses represent the change with  $k_1/2$ ,  $k_2/5$ , and  $k_3/2$  k-points and the slope (ppm/mRy) describing the dependency on the Fermi smearing. For better comparison, the experimental<sup>19,21,22</sup> and theoretical shifts  $\delta_{\text{exp}}$  and  $\delta_{\text{theo}}$  (obtained from the least squares fit given in Figure 1) are also listed.

to 2537(108) ppm, and the slope is  $-1.02(6)$ , close to the required value of  $-1$ . We have excluded YMg and YZn from the linear regression fit because the results for the two CsCl-type compounds are apparently completely off. Possible reasons for this will be discussed later.

A decomposition of the theoretical shielding into orbital ( $\sigma_o$ ), spin contact ( $\sigma_c$ ), and spin-dipolar terms ( $\sigma_{\text{sd}}$ ) is shown in Table 2 and Figure 2. For most compounds the Fermi contact term  $\sigma_c$  is the major component and sets the general trend with variations of up to 3000 ppm, but  $\sigma_o$  is not constant either and varies up to 1500 ppm. Neither  $\sigma_o$  nor  $\sigma_c$  alone shows a good correlation with experimental shieldings (Figure 2), but it is the sum of these two terms which is essential. The spin dipolar contribution  $\sigma_{\text{sd}}$  is in most cases small and less than 200 ppm (and often even much smaller), except in very asymmetric compounds like YCo<sub>2</sub>Si<sub>2</sub> or YRu<sub>2</sub>Si<sub>2</sub>, where it can reach as much as 320 ppm.

Let us now analyze the spin contact term in more detail. It is quite apparent (Figure 2) that the spin contact term  $\sigma_c$  is not

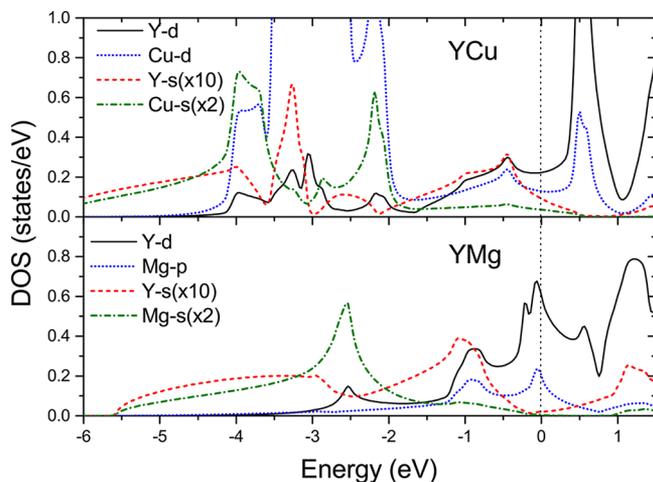


**Figure 2.** Correlation of the theoretical orbital ( $\sigma_o$ , blue diamonds) and spin contact ( $\sigma_c$ , red triangles) components of the shielding with the measured shifts ( $\delta_{\text{exp}}$ ).

always negative (paramagnetic) as expected for a metal if we consider only the simple picture of reoccupation of Y-5s states around  $\epsilon_F$  as the origin of the induced spin density. Instead, it



their DOS at  $\epsilon_F$  that comes predominantly from Y-4d states. In Figure 7 we compare the PDOS of YMg (problematic case)

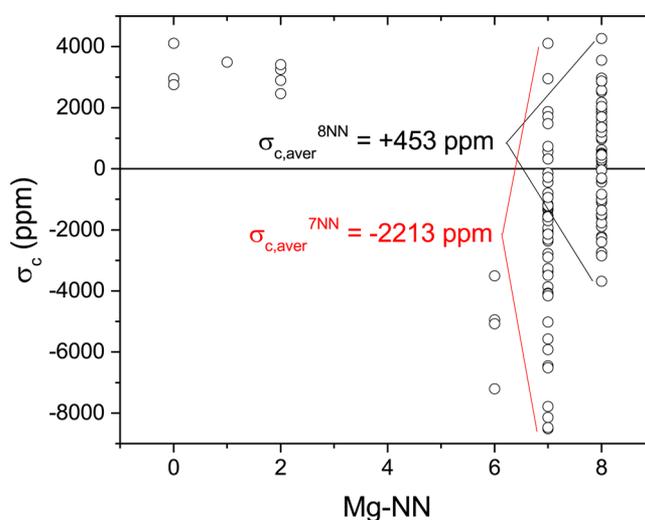


**Figure 7.** Y-5s and 4d PDOS (states/eV) together with Mg-3s and 3p PDOS in YMg (bottom) and with Cu-4s and 3d PDOS in YCu (top). The corresponding s-PDOS are scaled by a factor 10 and 2 as indicated in the figure.

with that of YCu (unproblematic). While for YMg the Y-4d (and the hybridized Mg-3p) PDOS has a large peak at  $\epsilon_F$ , the corresponding PDOS for YCu is flat and much smaller. On the other hand, the Y-5s (Mg-3s) PDOS, which is responsible for the valence  $\sigma_c$ , is nearly zero in YMg but sizable in YCu. The external magnetic field induces in YMg a large Y-4d moment ( $0.014 \mu_B/100$  T) leading to a gigantic core polarization and a huge diamagnetic contribution to the shielding ( $\sigma_c > 0$ ), while the valence  $\sigma_c$  is nearly zero. On the contrary, for YCu the induced Y-4d moment ( $0.002 \mu_B/100$  T) and the corresponding core polarization are small, but the valence  $\sigma_c$  is strongly paramagnetic. In cases with a large (and strongly varying) DOS at  $\epsilon_F$  the results are very sensitive to k-mesh, but we can converge  $\sigma_c$  with grids of  $10^6$  k-points. Moreover, the Fermi smearing parameter  $k_B T$  has a significant influence on the results as evidenced by the huge slope  $d\sigma_c/d(k_B T)$  for those compounds (Table 2). This means that the chosen value of the smearing may influence the results by more than 1000 ppm. We also found a large change of the results ( $\sigma_c$  about 30% smaller) when using the local density approximation (LDA) instead of the PBE-GGA. It is well-known that GGAs can overestimate magnetism,<sup>7–9</sup> but even within LDA we do not find a meaningful magnetic shielding, although the discrepancies decrease slightly. In any case, all these effects cannot fully account for the discrepancies between theory and experiment, except when we would blame DFT to be very wrong for these particular cases.

Alternatively, we note that for many intermetallic compounds (with CsCl structure) the preparation of stoichiometric and fully ordered materials is very difficult. Obviously, non-stoichiometry would change the number of valence electrons and could move  $\epsilon_F$  away from the pronounced peak. In addition (partial) disorder breaks the long-range order and removes the flat bands near the Fermi level, changing the overall shape of the DOS. The latter proposal was tested with a  $4 \times 4 \times 4$  supercell containing 128 atoms (64 Y and 64 Mg). Four Y and 4 Mg positions were chosen randomly (and in two different ways), and their occupations were changed to the antisite atom.

After structural relaxation (large displacements due to the very different sizes of Mg and Y) the induced spin contact hyperfine fields due to an external magnetic field were calculated. The 64 Y atoms in both supercells show vastly different magnetic shieldings depending on their environment. Y atoms keeping their (little distorted) 8 NN Mg neighbors show mostly a rather large positive  $\sigma_c$  similar to the ordered compound (on average +453 ppm as compared to +2502 ppm in ordered YMg), while Y atoms with a mixed Y and Mg-NN environment tend to get negative shieldings. A distribution of the 64 Y –  $\sigma_c$  in these two particular supercells and their relation to the number of Mg-NN is shown in Figure 8. Obviously, the 4 antisite Y atoms with



**Figure 8.** Distribution of Y  $\sigma_c$  in 2 different 128 atom supercells with 4 Mg and 4 Y randomly chosen antisite positions as a function of the Mg-NN atoms for the corresponding Y atoms. The Y antisite atoms have 0, 1, and 2 Mg NN, respectively, and the Y atoms with 8 Mg-NN have no direct Y antisite neighbor and (slightly distorted) original coordination. The average shielding for 7 and 8 Mg-NN is also given in the figure.

0, 1, or 2 Mg-NN in our model do not have a suitable magnetic shielding, but the many Y sites (one Mg antisite atom affects 8 Y sites) with 7 Mg and 1 Y NN have a negative  $\sigma_c$  with an average of  $-2213$  ppm, which would bring the magnetic shielding in qualitative agreement with the experimentally observed shifts.

For the carbide YCoC the agreement with experiment is not overwhelming ( $\Delta\delta$  about 670 ppm), but owing to the fact that one expects large amounts of C vacancies<sup>24</sup> in this structure, it is not too bad either.

## SUMMARY AND CONCLUSION

Solid-state NMR calculations based on DFT have been used to examine the NMR shielding in various intermetallic yttrium compounds. These calculations can reproduce the experimentally observed shifts very well except for two simple structures, YMg and YZn. These discrepancies originate from a large Y-4d PDOS at the Fermi energy, and the corresponding large induced Y spin magnetic moments lead to big diamagnetic Fermi contact terms ( $\sigma_c > 0$ ) due to core polarization. The reasons for these discrepancies with experiment could have a few origins. For instance, it could be a problem of DFT which overestimates magnetism in certain cases, partly because spin fluctuations are ignored. However, we believe that the

experimental samples might not be fully ordered. Calculations for a disordered YMg alloy model indicate that Y atoms with Y antisite atoms next to them have on average a  $\sigma_c$  that is 4000 ppm more negative, and this would bring the theoretical shieldings in line with the experimentally observed shift and support our proposal that the experimental samples might not be perfectly ordered.

In most compounds the chemical trends are mainly due to the spin component of the response which is dominated by the contact term. In metals, the response of the valence *s* (*Y*-5*s*) wave functions to an external magnetic field leads to a paramagnetic response due to a reoccupation of spin-up and -down states giving rise to a negative spin contact term. However, when the *s*-PDOS at the Fermi level is small and the *d* PDOS is large, a diamagnetic response of the spin contact term can be observed because the induced 4*d* magnetic moment polarizes the core and semicore state in the opposite way. This possible cancellation can lead to total spin contributions which are as expected largely paramagnetic, but it can also give very small or even a strongly diamagnetic responses. On the other hand, the orbital shielding is by no means small or constant within the series but contributes significantly to the total shielding. The spin dipolar contribution is usually fairly small but in a few examples (YCo<sub>2</sub>Si<sub>2</sub> and YRu<sub>2</sub>Si<sub>2</sub>) can reach values up to 300 ppm.

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### Notes

The authors declare no competing financial interest.

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