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^{155}Gd isomer shifts. The case study: GdT_2Si_2

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Abstract. The experimentally obtained ^{155}Gd Mössbauer effect results in isomer shifts for GdT_2Si_2 compounds (where T are transition metals for the 3*d*, 4*d* and 5*d* series) are analysed in terms of charge-transfer effects and *s*, *d* redistribution by means of the extended Miedema and van der Woude model. The comparison between the theoretically predicted and measured values is discussed. Although these theoretical predictions of isomer shifts are in reasonable agreement with those found in the experiment, nevertheless they do not follow the experimental dependence on T metal acquired for each *nd*-series.

Key words: isomer shifts • Mössbauer studies • rare earth ternary compounds

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Introduction

The importance of isomer shift measurements is that they are sampling electron densities, mainly of *s*-character, at resonant nuclei embedded in a given material, giving fingerprint characteristic of different phases, compounds, crystallographic sites, etc. As it is seen from Fig. 1, the various isomer shifts of the gadolinium intermetallics cover a broad range and they strongly depend on the nature of the elements coordinating the gadolinium atoms.

A concise overview on the theoretical background of ^{155}Gd Mössbauer spectroscopy can be found in a review article by Czjzek [2] where some experimental results for intermetallic Gd compounds have already been included, reporting some data obtained till 1993. The latter review and an article by Silver and Withnall [11 and references therein] provide a good literature overview on ^{155}Gd data of different gadolinium-based oxides. Recent review [10] brings useful information on ^{155}Gd Mössbauer spectroscopy studies in intermetallic Gd compounds presenting results obtained after 1993.

In this work, the Mössbauer ^{155}Gd isomer shifts obtained experimentally [3] for the whole family of GdT_2Si_2 compounds, as the transition T metal is varied through the 3*d*-, 4*d*- and 5*d*-transition metal series, are examined. Using the extended Miedema and van der Woude model, developed for ternary alloys [5], the ^{155}Gd isomer shifts for GdT_2Si_2 itermetallics were calculated and critically compared with those measured in the experiment [3].

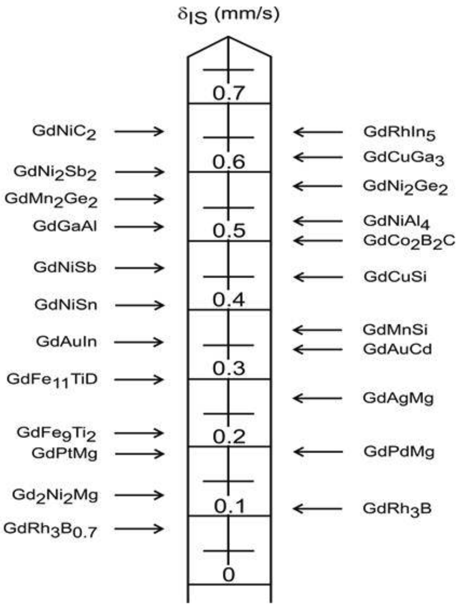

Fig. 1. Isomer shift scale (with respect to a ^{155}Eu:SmPd$_3$ source) for the 86.5 keV transition of a ^{155}Gd for selected intermetallic Gd compounds.

Isomer shifts observed for ^{155}Gd Mössbauer isotope

Information about electronic structure at Gd sites and its variation with atomic number of the given transition T metal Z_{nd} for GdT_2Si_2 compounds can be derived primarily from isomer shifts δ_{IS} and also from quadrupole splittings ΔE_Q (see Table 2 and Fig. 6 of Ref. [3]).

The isomer shift can be expressed in the form:

$$(1) \qquad \delta_{\mathrm{IS}} = \mathrm{const} \cdot \Delta < r^2 >_{\mathrm{nucl}} [\rho_{el}^{\mathrm{abs}}(0) - \rho_{el}^{\mathrm{source}}(0)]$$

where ρ stands for the electron densities, of mainly *s*-character, observed at ^{155}Gd nuclei for a given absorber material and a source used in Mössbauer experiment. Since the difference between the average squared nuclear radii in the excited and ground states $\Delta\langle r^2\rangle_{\mathrm{nucl}} = -(8 \pm 2) \cdot 10^{-18}\ \mathrm{m}^2$ [1] is for the $E_\gamma = 86.5$ KeV gamma transition in ^{155}Gd negative, the observed large positive isomer shifts are connected with a decrease of the total charge density at gadolinium Gd nuclei. If we accept $5d6s^2$ electron configuration of valence electrons for metallic gadolinium, this decrease can be caused either by the transfer of 6*s* electrons to the transition metal *d*-band or by an increase of occupation of 5*d* level at the Gd site. An increased atomic volume may also lead to a reduced electron density at the nuclei and thus to a more positive isomer shift. Both above-mentioned effects on the observed isomer shifts for GdT_2Si_2 series have already been discussed thoroughly in the Ref. [3], but in the present paper the extended Miedema-van der Woude semi-empirical model was applied to derive isomer shifts values.

Extended Miedema and van der Woude model

The total isomer shift $\delta_{\mathrm{IS}}^{\mathrm{calc}}$ for ^{155}Gd in the ternary Gd compounds represented by the formula GdM_mN_n can be composed as a sum of two terms [5]:

$$(2) \qquad \delta_{\mathrm{IS}}^{\mathrm{calc}} = \delta_{\mathrm{IS}}^{\mathrm{GdM}_m\mathrm{N}_n} = <\delta> + <C>$$

$$(3) \qquad <\delta> = \frac{m(f_{\mathrm{M}}^{\mathrm{Gd}})^2 \delta_{\max}^{\mathrm{Gd\text{-}M}} + n(f_{\mathrm{N}}^{\mathrm{Gd}})^2 \delta_{\max}^{\mathrm{Gd\text{-}N}}}{m f_{\mathrm{M}}^{\mathrm{Gd}} + n f_{\mathrm{N}}^{\mathrm{Gd}}}$$

$$(4) \qquad <C> = \frac{m f_{\mathrm{M}}^{\mathrm{Gd}} C(\mathrm{GdM}_{m+n}) + n f_{\mathrm{N}}^{\mathrm{Gd}} C(\mathrm{GdN}_{m+n})}{m f_{\mathrm{M}}^{\mathrm{Gd}} + n f_{\mathrm{N}}^{\mathrm{Gd}}}$$

$$(5) \qquad C(\mathrm{Gd}_x\mathrm{M}_{1-x}) = C' x f_{\mathrm{M}}^{\mathrm{Gd}}$$

All quantities in expressions (2)–(5) are defined in the Ref. [5] and references therein, but their definitions also appear below. For the majority of binary compounds, the values of isomer shifts $\delta_{\max}^{\mathrm{Gd\text{-}M}}$ and *C*' are given in Table 3 of that reference. The values of $\delta_{\max}^{\mathrm{Gd\text{-}M}}$ and *C*' for Gd-Ru, Gd-Os, which were not found during the literature search, and for Gd-Ir binary systems were calculated from the beginning using the formulas described in Refs. [5] and [6]:

$$(6) \qquad \delta_{\max}^{\mathrm{Gd\text{-}M}} = P'(\varphi_{\mathrm{M}}^* - \varphi_{\mathrm{Gd}}^*) + Q'(n_{\mathrm{WS}}^{\mathrm{M}} - n_{\mathrm{WS}}^{\mathrm{Gd}}) / n_{\mathrm{WS}}^{\mathrm{Gd}}$$

$$(7) \qquad C' = \lambda_V \frac{\Delta V_{\max}^{\mathrm{Gd}}}{V^{\mathrm{Gd}}} = \left[\frac{\partial \delta}{\partial \ln V}\right]_{\mathrm{Gd}} \cdot \frac{\Delta V_{\max}^{\mathrm{Gd}}}{V^{\mathrm{Gd}}}$$

The first term in Eq. (6) accounts for the charge transfer from Gd to M, while the second one is associated with the intra-atomic *d*-*s* conversion during alloying of Gd with another metal. According to Ref. [6]: $P' = +0.36(2)\ \mathrm{mm\cdot s^{-1}\cdot V^{-1}}$, $Q' = -0.18(2)\ \mathrm{mm\cdot s^{-1}}$ and $\lambda_V = 1\ \mathrm{mm\cdot s^{-1}}$. The expression for $\Delta V_{\max}^{A}$ (for a given binary alloy *AB*; in our case *A* = Gd and *B* is a metal T or Si, respectively) is given in Ref. [8] and takes the form:

$$(8) \qquad \Delta V_{\max}^{\mathrm{Gd}} = \frac{-P_0 f_B^A V_A^{2/3} (\varphi_B^* - \varphi_A^*)}{(n_{\mathrm{WS}}^A)^{-1/3} + (n_{\mathrm{WS}}^B)^{-1/3}} [(n_{\mathrm{WS}}^A)^{-1} - (n_{\mathrm{WS}}^B)^{-1}]$$

where $P_0 = 1.5$ [8], f_B^A is a correction factor defined in [5, 9] being a measure of the fractional area of contact between Gd atom with M atoms, φ^* is the electronegativity and n_{WS} stands for the electron density at the Wigner-Seitz atomic cell boundaries in pure metal *A* or *B*, respectively. The numerical values for φ^* and n_{WS} for Gd, Ru and Ir as well as for other elements can be found, for instance, in Refs. [4, 7]. It is worth of noting that the recalculated values of $\delta_{\max}^{\mathrm{Gd\text{-}M}}$ for other binary systems needed here were found to be in perfect agreement with those presented in Table 3 of Ref. [5] except the value for Gd-Ir system, for which remarkable discrepancy was found. Table 1 consists of the calculated values of $\delta_{\max}^{\mathrm{Gd\text{-}M}}$ and *C*' for Gd-Ru, Gd-Os and Gd-Ir binary systems, while the calculated values of ^{155}Gd isomer shifts $\delta_{\mathrm{IS}}^{\mathrm{calc}}$ for GdT_2Si_2 (T = 3*d*, 4*d* and 5*d*

Table 1. Calculated values of $\delta_{\max}^{\mathrm{Gd\text{-}M}}$ and C' for Gd-Ru, Gd-Os and Gd-Ir binary systems

System	$\delta_{\max}^{\mathrm{Gd\text{-}M}}$ (mm/s)	*C*' (mm/s)
Gd-Ru	0.349	–0.337
Gd-Os	0.328	–0.343
Gd-Ir	0.403 0.600$^+$	–0.361 –0.496$^+$

$^+$ These values are given in Table 3 of Ref. [5].

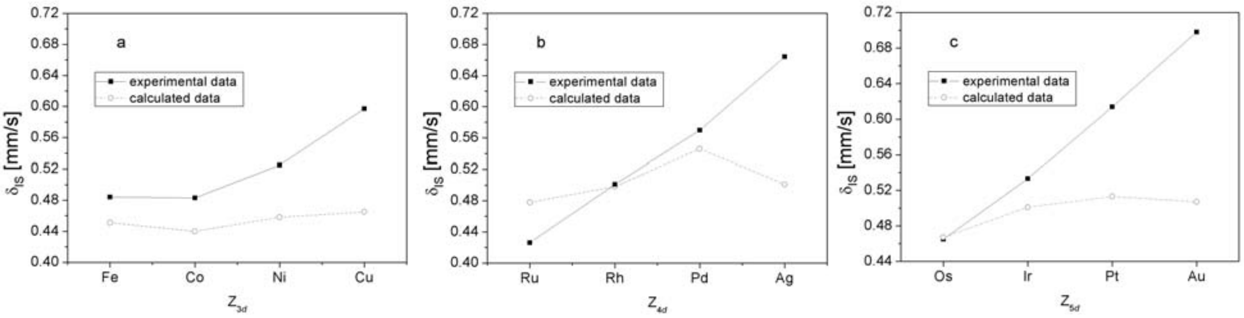

Fig. 2. Comparison of the calculated and experimental [3] ^{155}Gd isomer shifts (with respect to ^{155}Eu:$SmPd_3$ source) for GdT_2Si_2 (T = 3*d*, 4*d* and 5*d* transition metals) intermetallic compounds, vs. Z_{nd}, for (a) 3*d*, (b) 4*d* and (c) 5*d* series, respectively.

Table 2. Comparison of the data calculated from the extended Miedema and van der Woude model and the experimental ^{155}Gd Mössbauer isomer shifts for GdT_2Si_2 (T = 3*d*, 4*d* and 5*d* transition metals) [3] intermetallic compounds

Compound	$<\delta>$ (mm/s)	$<C>$ (mm/s)	$\delta_{IS}^{calc} = <\delta> + <C>$ (mm/s)	δ_{IS}^{exp} (mm/s) [3]
$GdMn_2Si_2$	0.481	–0.056	0.426	0.492(2)
$GdFe_2Si_2$	0.515	–0.064	0.451 0.45^+	0.484(2) 0.480^+
$GdCo_2Si_2$	0.507	–0.067	0.440	0.483(3)
$GdNi_2Si_2$	0.527	–0.069	0.458	0.525(1)
$GdCu_2Si_2$	0.522	–0.057	0.465	0.597(2)
$GdRu_2Si_2^*$	0.540	–0.062	0.478	0.0426(4)
$GdRh_2Si_2$	0.572	–0.074	0.498 0.50^+	0.501(4) 0.450^+
$GdPd_2Si_2$	0.621	–0.075	0.546	0.570(5)
$GdAg_2Si_2$	0.566	–0.055	0.501	0.664(3)
$GdOs_2Si_2^*$	0.530	–0.063	0.467	0.465(7)
$GdIr_2Si_2^*$	0.566 0.658°	–0.065 –0.077°	0.501 0.581°	0.533(4)
$GdPt_2Si_2$	0.580	–0.067	0.513	0.614(5)
$GdAu_2Si_2$	0.576	–0.069	0.507	0.698(6)

All calculated values presented in this table were obtained according to the method developed in Ref. [5].
$^+$ These values were taken from Table 2 of Ref. [5].
* Calculations were made from the beginning as described in the text.
° These results were obtained using $\delta_{max}^{Gd\text{-}M}$ = 0.600 mm/s and C' = –0.496 mm/s (Table 3 of Ref. [5]), which differ remarkably from the respective values obtained in this work (Table 1).

transition metals) intermetallic compounds with the use of the expressions (2)–(8) are gathered in Table 2 where, for comparison, the experimental values of isomer shifts δ_{IS}^{exp} obtained in Ref. [3] are also included. This comparison is illustrated in Fig. 2.

Discussion and conclusions

It is clearly seen from Table 2 that the extended model of Miedema and van der Woude gives large positive isomer shifts in reasonable good agreement with those found in the experiment [3]. The strong monotonous increase of the experimental isomer shifts with atomic number Z_{nd}, which is particularly pronounced for the 4*d* and 5*d* rows, however, it is not followed by the model results presented in Fig. 2. For the compounds with noble metals, for example, this model predicts isomer shifts which are less positive than those in the compounds with transition T metals at the beginning of the series (Fe, Ru, Os).

References

1. Bauminger E-R, Kalvius G-M, Wagner F-E (1978) Isomer shifts in the rare earth. In: Shenoy G-K, Wagner F-E (eds) Mössbauer isomer shifts. North-Holland Publishing, Amsterdam, pp 661–756
2. Czjzek G (1993) Mössbauer spectroscopy of new materials containing gadolinium. In: Long G-J, Grandjean F (eds) Mössbauer spectroscopy applied to magnetism and materials science. Plenum Press, New York, Vol. 1, pp 373–429
3. Czjzek G, Oestreich V, Schmidt H, Łątka K, Tomala K (1989) A study of compounds GdT_2Si_2 by Mössbauer spectroscopy and by bulk magnetization measurements. J Magn Magn Mater 79:42–56
4. de Graaf H, Thiel RC, Buschow KHJ (1982) Charge transfer and ^{155}Gd isomer shift in various intermetallic compounds of Gd. J Phys F 12:2079–2090
5. de Vries JWC, Thiel RC, Buschow KHJ (1985) ^{155}Gd Mössbauer effect and magnetic properties of some ternary gadolinium intermetallic compounds. J Less-Common Met 111:313–320

6. de Vries JWC, Thiel RC, Buschow KHJ (1985) Volume effects on the Mössbauer isomer shift in intermetallic compounds containing gadolinium. J Phys F 15:1413–1426
7. Miedema AR, de Chatel PF, de Boer FR (1980) Cohesion in alloys – fundamentals of semi-empirical model. Physica B 100:1–28
8. Miedema AR, Niessen AK (1982) Volume effects upon alloying of two transition metals. Physica B 114:367–374
9. Miedema AR, van der Woude F (1980) A cellular atomic model for the Mössbauer isomer shift of ^{197}Au in alloys. Physica B 100:145–156
10. Pöttgen R, Łątka K (2010) ^{155}Gd Mössbauer spectroscopy on intermetallics – an overview. Z Anorg Allg Chem 636:2244–2255
11. Silver J, Withnall R (2004) Probes of structural and electronic environments of phosphor activators: Mössbauer and Raman spectroscopy. Chem Rev 104:2833–2855