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Michael Kuz'min, Manuel Richter. Lanthanide exchange fields and intermultiplet transitions in permanent-magnet materials. The European Physical Journal Plus, 2023, 138 (11), pp.1068. 10.1140/epjp/s13360-023-04449-5 . hal-04524783

HAL Id: hal-04524783

<https://hal.science/hal-04524783>

Submitted on 28 Mar 2024

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Lanthanide Exchange Fields and Intermultiplet Transitions in Permanent-Magnet Materials

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Received: date / Revised version: date

Abstract. Intermultiplet (spin-orbit) transitions in lanthanides, observed by means of high-energy inelastic neutron scattering are well-suited for the determination of exchange field H_{ex} in permanent-magnet materials. The situation is particularly favorable in Nd-based magnets, where H_{ex} is given by $\mu_B H_{\text{ex}} = \frac{143}{296}(E_{\text{inter}} - \Delta_{\text{so}})$, E_{inter} being the observed transition energy and Δ_{so} the spin-orbit splitting between the barycenters of the two lowest-lying multiplets. The latter can be regarded as a known atomic constant, $\Delta_{\text{so}} = 232 \pm 1$ meV. A more accurate value of Δ_{so} is obtainable by way of relativistic density-functional calculations, however, it proves material-dependent. Thus, $\Delta_{\text{so}} = 231.4$ meV for Nd₂Fe₁₄B. Two obstacles in the way of the direct determination of H_{ex} are J -mixing and crystal electric field. In order to allow for the J -mixing, approximate formulas are proposed that enable a definitive solution of the problem. By contrast, crystal-field corrections have to be treated on a case-by-case basis.

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1 Introduction

Inelastic neutron scattering (INS) is a powerful spectroscopic tool equally applicable to metals and insulators, without alternative in the former case. Especially low-energy INS is widely used for the investigation of lanthanide spectra in metals at excitation energies not exceeding ~ 30 meV. (This boundary is somewhat arbitrary and corresponds to room temperature.) By means of this technique one often succeeds in determining the crystal-field (CF) splitting of the ground J -multiplet and determining CF parameters [1,2,3], for a review see [4]. As against that, the use of high-energy INS for the study of spectra at and above ~ 100 meV has been far less successful. After the initial reports of observation of intermultiplet (spin-orbit) transitions in Pr and Nd compounds [5,6] the progress slowed down and came to a standstill. The reason is lack of new physically significant results able to justify the laborious and expensive experimentation. Such course of events was largely due to the poor choice of the objects of investigation – simple lanthanide-rich model systems. It turns out that structural simplicity is no guarantee of a simple INS spectrum. The latter is simplified in the following two opposite limits.

(i) CF-dominated lanthanide spectra in systems without magnetic ordering or with a low ordering temperature such that $kT_{\text{ord}} \ll \Delta_{\text{CF}}$, where Δ_{CF} stands for the splitting between the ground and the first excited CF levels. It is vital for successful interpretation that the local symmetry of the lanthanide site be possibly high. And it goes without saying that all measurements should be carried out at $T > T_{\text{ord}}$.

(ii) Exchange-dominated spectra, $\mu_B H_{\text{ex}} \gg \Delta_{\text{CF}}$. In this case the multiplet splitting patterns are approximately equidistant and the large INS linewidth (~ 10 meV) is no obstacle for resolving the individual levels. Besides, the choice of temperature presents no difficult task. For example, $T = 4.2$ K is an excellent a priori choice that guarantees thermal depopulation of all excited levels, $kT \ll \mu_B H_{\text{ex}}$. Moreover, the simplicity of the lanthanide eigenstates, $|JM\rangle$, results in a particularly simple spectrum of intermultiplet transitions out of the ground state, with a single dominant line having a chance of being observed. Finally, a decisive advantage of exchange-dominated systems is a simple linear relation between the observed energy of the intermultiplet transition, E_{inter} , and the exchange field on the lanthanide, H_{ex} , cf. Eqs. (5) below.

The exchange-dominated paradigm is realized in modern permanent-magnet materials. These are iron- or cobalt-rich intermetallic compounds with light lanthanides. The exchange field H_{ex} amounts to several megaoersteds and

plays an important role: it determines how quickly magnetic anisotropy (and coercivity) decays with temperature. At and above room temperature the main contribution to the anisotropy falls off as $(\mu_B H_{\text{ex}}/kT)^2$ [7]. It is therefore essential to have a possibly precise knowledge of H_{ex} . However, H_{ex} is not a directly observable quantity. Rather, it is determined – together with many other adjustable parameters – by non-linear fitting of magnetization data [8, 9, 10]. The problem is ill-conditioned and the results are scattered [11]. The want of a reliable and accurate spectroscopic technique for the determination of H_{ex} in permanent magnets is evident. But intermultiplet transitions observed by high-energy INS provide just the technique sought, for H_{ex} is then given by one of the linear expressions (5) in terms of the observed transition energy E_{inter} .

The only question is: How accurate are the linear expressions (5)? This work aims at giving a detailed answer to this question. In our approach we shall stay within the framework of the Russel-Saunders approximation since (i) H_{ex} is sought for subsequent use as a parameter in models limited to the same approximation and (ii) the approximation itself is a fair one, as long as one does not go beyond the first excited J -multiplet [12]. The paper is organised as follows: Eqs. (5) are introduced in Section 2 (as three particular forms of the same expression, corresponding to R=Pr, Nd, Sm) and their main limitations are considered in Sections 2–4. Section 5 then briefly addresses the subject of sample quality – not usually recognised as a major obstacle in the way of high-energy INS but in fact well able to preclude the observation of an intermultiplet transition in an iron- or cobalt-rich intermetallic compound. Section 6 concludes the paper.

2 Allowance for J -Mixing

Two decades ago we advocated the neglect of J -mixing when interpreting the intermultiplet transitions in Sm compounds [13] on the grounds that its contribution did not exceed 1 meV, while the transition energies were known to ± 2 meV. This neglect now seems unjustified and unnecessary and we would like to improve on that point.

The most intense intermultiplet transition takes place between the ground state $|JM\rangle$ of the light rare earth, with $M = J = L - S$, and the lowest state $|J'M'\rangle$ of the first excited multiplet, having $M' = J' = J + 1$. The multiplets are split by an exchange field H_{ex} acting on the rare earth. The energy gap between the two multiplets, denoted by Δ_{so} , is due to spin-orbit coupling. Regarding the operator $2\mu_B H_{\text{ex}} S_z$ as a perturbation with respect to the spin-orbit coupling, one gets in the case of Sm [13]:

$$E_{\text{inter}} = \Delta_{\text{so}} + \frac{148}{63} \mu_B H_{\text{ex}} + E_{J\text{mix}} \quad (1)$$

with

$$E_{J\text{mix}} = 0.8773 \frac{(\mu_B H_{\text{ex}})^2}{\Delta_{\text{so}}} - 6.178 \frac{(\mu_B H_{\text{ex}})^3}{\Delta_{\text{so}}^2} + \dots \quad (2)$$

Thus, $E_{J\text{mix}}$ comprises corrections of order higher than one in $\mu_B H_{\text{ex}}$. If $E_{J\text{mix}}$ could be neglected, Eq. (1) would acquire a particularly simple form, with just a constant and a linear term,

$$E_{\text{inter}} = \Delta_{\text{so}} + \frac{148}{63} \mu_B H_{\text{ex}}. \quad (3)$$

The numerical prefactor of the second term is an increment of the quantity $2J(g_J - 1)$ between the ground and the first excited multiplets of Sm,

$$2J(g_J - 1) \Big|_{J=5/2}^{J=7/2} \quad (4)$$

the relevant Landé factors being $g_{5/2} = \frac{2}{7}$ and $g_{7/2} = \frac{52}{63}$. Equation (3) would make the observation of intermultiplet transitions a powerful tool for the determination of H_{ex} . The procedure appears rather straightforward:

$$\mu_B H_{\text{ex}} = \frac{63}{148} (E_{\text{inter}} - \Delta_{\text{so}}) \quad (5.\text{Sm})$$

where E_{inter} is determined from experiment and Δ_{so} is a known constant. Thus, $\Delta_{\text{so}} = 130$ meV in the case of Sm (see Section 4 for more details).

Unfortunately, the perturbation series (2) breaks down for $H_{\text{ex}} \gtrsim 2$ MOe (see Fig. 1) and is unsuitable for Fe- and Co-rich Sm compounds, whose H_{ex} is typically between 3 and 4 MOe. The accuracy of Eq. (3), based on the neglect of $E_{J\text{mix}}$, is potentially compromised.

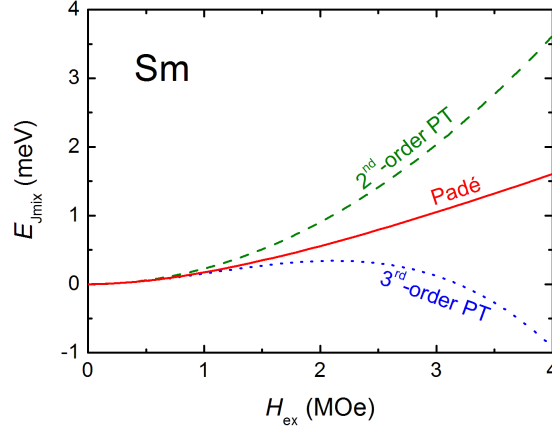


Fig. 1. J -mixing correction to the ${}^6H_{5/2} \rightarrow {}^6H_{7/2}$ transition energy in Sm as given by the perturbation theory polynomials (2) and a [2,1] Padé approximant (11.Sm).

In the remaining part of this Section we shall consider J -mixing in more detail, with a view to finding an alternative expression for $E_{J\text{mix}}$, which (i) would be more accurate than Eq. (2) and (ii) which could be included in the final formula for H_{ex} rather than neglected. We begin by a special case of praseodymium, which due to its low multiplicity, $2S + 1 = 3$, permits an exact expression for $E_{J\text{mix}}$, without recourse to perturbation theory.

2.1 Praseodymium: a case study

The low multiplicity of the ground term 3H of praseodymium implies that, within the term, the full diagonalisation of the Hamiltonian under consideration,

$$\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S} + 2\mu_B H_{\text{ex}} S_z \quad (6)$$

necessitates the solution of cubic equations at the most. Both terms of the Hamiltonian (6) are diagonal in the quantum numbers M , but only the first term (spin-orbit coupling) is diagonal in J . As regards the second term of Eq. (6), containing the exchange field H_{ex} and the operator S_z , it has nonzero matrix elements of two kinds: $\langle JM | \dots | JM \rangle$ and $\langle JM | \dots | J \pm 1, M \rangle$. In the case of Pr the ground state of \mathcal{H} belongs to a 3×3 block ($M = 4$ and $J = 4, 5, 6$), whereas the final state of the intermultiplet transition ${}^3H_4 \rightarrow {}^3H_5$ belongs to a 2×2 block ($M = 5$, $J = 5$ and 6). The matrix elements of S_z are given by Eqs. (87,88) of Ch. VI of Ref. [14]. For setting the matrices one further needs the spin-orbit splittings between 3H_4 and 3H_5 ($\Delta_{\text{so}} = 5\lambda$) and between 3H_5 and 3H_6 ($\Delta'_{\text{so}} = 6\lambda$). The former is regarded as an independent parameter known from experiment; the latter is related to the former by the Landé interval rule: $\Delta'_{\text{so}} = \frac{6}{5}\Delta_{\text{so}}$. For each matrix block the lowest eigenvalue is sought. In the end, one arrives at an expression for the transition energy, similar to Eq. (1) but adapted for Pr,

$$E_{\text{inter}} = \Delta_{\text{so}} + \frac{29}{15} \mu_B H_{\text{ex}} + E_{J\text{mix}} \quad (7)$$

Here the numerical prefactor of the second term is a combination similar to (4) of the Landé factors $g_4 = \frac{4}{5}$ and $g_5 = \frac{31}{30}$. The entire nonlinear dependence on H_{ex} is concentrated in the last term of Eq. (7),

$$E_{J\text{mix}} = \Delta_{\text{so}} f\left(\frac{\mu_B H_{\text{ex}}}{\Delta_{\text{so}}}\right) \quad (8)$$

where $f(\eta)$ stands for a function defined as follows:

$$f(\eta) = -\frac{7}{15} - \frac{14}{15}\eta - \frac{1}{5}\sqrt{9 + 20\eta + 25\eta^2} - \frac{2}{15}\sqrt{91 + 240\eta + 300\eta^2} \\ \times \cos\left(\frac{2\pi}{3} + \frac{1}{3}\arccos\frac{136 - 180\eta - 900\eta^2}{(91 + 240\eta + 300\eta^2)^{3/2}}\right) \quad (9)$$

This expression originates from exact (within the ground LS -multiplet) diagonalisation of the Hamiltonian (6); its validity is not limited to η small. The presentation in Figure 2 is however restricted to $H_{\text{ex}} < 6$ MOe. This range is

on the one hand largely sufficient for the systems of our interest, which all have $H_{\text{ex}} \lesssim 4$ MOe. On the other hand, within this range J -mixing is still relatively weak, $\mu_B H_{\text{ex}} \ll \Delta_{\text{so}}$, and J remains a 'good' quantum number suitable at least for labelling the energy levels.

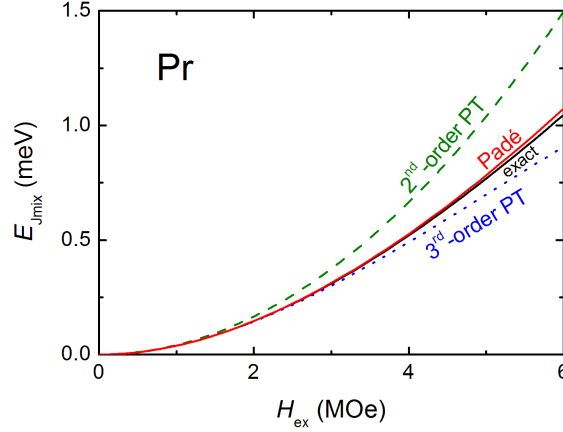


Fig. 2. The same as Figure 1 but for the ${}^3H_4 \rightarrow {}^3H_5$ transition in Pr. The exact result given by Eqs. (8, 9) is shown as well.

The continuous curve labelled 'exact' in Figure 2 presents the $E_{\text{Jmix}}(H_{\text{ex}})$ dependence as given by Eqs. (8, 9). One concludes that as far as Pr compounds are concerned, $E_{\text{Jmix}} \lesssim 0.5$ meV and so J -mixing can be neglected, given the current state of knowledge of E_{inter} (± 2 meV). In the light of this finding, it may appear that our research is of purely academic interest. This is not true for at least two reasons. Firstly, experimental resolution is nearly certain to improve in the future. Secondly, we wish to work out a technique applicable to other rare earths, in particular to Sm, where J -mixing is especially strong and no exact analytical diagonalisation is possible. It is therefore instructive to compare Eqs. (8,9) with simpler approximate expressions. Our next step is to expand $f(\eta)$ in a power series, either directly or by using the perturbation theory. The following expression for E_{Jmix} results:

$$E_{\text{Jmix}} = 0.3225 \frac{(\mu_B H_{\text{ex}})^2}{\Delta_{\text{so}}} \left[1 - 2.951 \frac{\mu_B H_{\text{ex}}}{\Delta_{\text{so}}} + \dots \right] \quad (10)$$

This is quite similar to Eq. (2) but adapted for Pr. A small distinction is that the leading term is factored out in Eq. (10). The accuracy of the expansion (10) can be judged from Figure 2, where two curves should be viewed in particular: (i) that which presents the second-order term alone (i.e., the prefactor of the square bracket – dashed line) and (ii) the one given by the second- and third-order terms together (dotted line). The latter one is quite close to the exact result and fully sufficient as long as $R=\text{Pr}$ and $H_{\text{ex}} < 4$ MOe. Yet, a still more accurate expression can be obtained at no extra cost, by simply rewriting Eq. (10) as a Padé approximant. Moving the square bracket into the denominator, one has

$$E_{\text{Jmix}} = \frac{0.3225 (\mu_B H_{\text{ex}})^2}{\Delta_{\text{so}} + 2.951 \mu_B H_{\text{ex}}} \quad (11.\text{Pr})$$

The resulting $E_{\text{Jmix}}(H_{\text{ex}})$ dependence – the red continuous line in Fig. 2 – lies closer to the exact curve than the second- and third-order polynomials. Moreover, the Padé approximant (11.Pr) remains good-tempered at higher H_{ex} , where the polynomial approximation inevitably breaks down.

An added advantage of Eq. (11.Pr) is that when it is set in Eq. (7) the resulting equation is readily solved for $\mu_B H_{\text{ex}}$:

$$\mu_B H_{\text{ex}} = 0.2448 E_{\text{inter}} - 0.4051 \Delta_{\text{so}} + \sqrt{0.05992 E_{\text{inter}}^2 - 0.03246 E_{\text{inter}} \Delta_{\text{so}} - 0.00174 \Delta_{\text{so}}^2} \quad (12.\text{Pr})$$

This formula does not require any additional information and is not much more difficult to use than Eq. (5) adapted for Pr,

$$\mu_B H_{\text{ex}} = \frac{15}{29} (E_{\text{inter}} - \Delta_{\text{so}}) \quad (5.\text{Pr})$$

The formal advantage of Eq. (12.Pr) is that it does take into account J -mixing, whereas Eq. (5.Pr) does not. Taking $E_{\text{inter}} = 300$ meV as a typical example and $\Delta_{\text{so}} = 260$ meV as deduced from optical data in Section 4.2, one finds $H_{\text{ex}} = 3.57$ MOe from Eq. (5.Pr) and $H_{\text{ex}} = 3.53$ MOe from Eq. (12.Pr). The difference cannot be viewed as significant, as long as both E_{inter} and Δ_{so} are precise to ± 2 meV and so H_{ex} is only 10% accurate.

2.2 Extension to other light rare earths

We shall concentrate on Sm and Nd, because of their importance for permanent-magnet materials. Writing the formulas presents no difficult task; no secular equations need to be solved, the standard perturbation theory can be used instead. The initial state of the intermultiplet transition is $|JJ\rangle$, with $J = 5/2$ for Sm and $J = 9/2$ for Nd, while the final state is $|J+1, J+1\rangle$. Second- and third-order corrections to the energy of each one of these two states arise from interaction with just one further state. Thus, $|JJ\rangle$ interacts with $|J+1, J\rangle$, situated Δ_{so} higher in energy. (By definition, Δ_{so} is the spin-orbit splitting between the ground and the first excited multiplets.) As regards the final state $|J+1, J+1\rangle$, it communicates with $|J+2, J+1\rangle$; the corresponding excitation energy is $\Delta'_{\text{so}} = \frac{J+2}{J+1}\Delta_{\text{so}}$ according to the Landé interval rule. As a result, one arrives at the following analogues of Eq. (11.Pr):

$$E_{\text{Jmix}} = \frac{0.8773 (\mu_{\text{B}} H_{\text{ex}})^2}{\Delta_{\text{so}} + 7.042 \mu_{\text{B}} H_{\text{ex}}} \quad (11.\text{Sm})$$

and

$$E_{\text{Jmix}} = \frac{0.2129 (\mu_{\text{B}} H_{\text{ex}})^2}{\Delta_{\text{so}} + 5.741 \mu_{\text{B}} H_{\text{ex}}} \quad (11.\text{Nd})$$

Calculations have been necessary for Eq. (11.Nd) only, Eq. (11.Sm) being a mere rewriting of Eq. (2). Setting the above expressions in Eq. (1) or in its adaptation for Nd (factor $\frac{296}{143}$ rather than $\frac{148}{63}$) and solving for $\mu_{\text{B}} H_{\text{ex}}$, one obtains expressions similar to Eq. (12.Pr):

$$\mu_{\text{B}} H_{\text{ex}} = 0.2021 E_{\text{inter}} - 0.2695 \Delta_{\text{so}} + \sqrt{0.04085 E_{\text{inter}}^2 - 0.05156 E_{\text{inter}} \Delta_{\text{so}} + 0.01525 \Delta_{\text{so}}^2} \quad (12.\text{Sm})$$

and

$$\mu_{\text{B}} H_{\text{ex}} = 0.2373 E_{\text{inter}} - 0.3229 \Delta_{\text{so}} + \sqrt{0.05631 E_{\text{inter}}^2 - 0.07057 E_{\text{inter}} \Delta_{\text{so}} + 0.02157 \Delta_{\text{so}}^2} \quad (12.\text{Nd})$$

These should be regarded as improved, corrected for J -mixing versions of the simple linear relations, Eq. (5.Sm) and its adaptation for Nd,

$$\mu_{\text{B}} H_{\text{ex}} = \frac{143}{296} (E_{\text{inter}} - \Delta_{\text{so}}) \quad (5.\text{Nd})$$

In order to better understand the interrelation of the corrected (12) and uncorrected (5) expressions for H_{ex} , let us turn back to Figures 1 & 2 and also consider a similar graph for Nd, Figure 3. Our first observation concerns the breakdown of the usual, polynomial-based perturbation theory. For H_{ex} between 3 and 4 MOe, the breakdown is an accomplished fact for both Sm and Nd, the advantage of the Padé approximants (11) being incontestable. For Pr the breakdown takes place above 6 MOe; below 4 MOe the third-order polynomial (10) is nearly as good as the Padé approximant (11.Pr). Since the Padé approximant is the best choice for all three elements, it is reasonable that one should adopt for general use Eqs. (11) as well as the thence derived Eqs. (12).

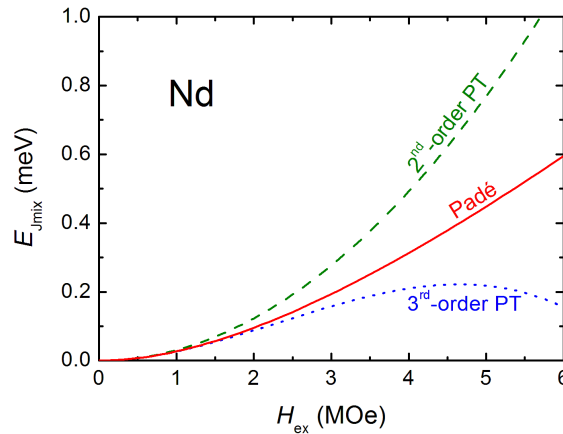


Fig. 3. The same as Figure 1 but for the ${}^4I_{9/2} \rightarrow {}^4I_{11/2}$ transition in Nd; $\Delta_{\text{so}} = 232$ meV.

The second consideration concerns the size of the J -mixing correction, whether it is worth taking into account at all. For Sm, where $E_{J\text{mix}} \sim 1$ meV, it is perhaps justified, given the current state of experimental precision (± 2 meV in both E_{inter} and Δ_{so}). But for Pr – and even more so for Nd – the effect appears too weak. In our view, the corrected expressions (12) should be used *in all cases*. Doing so requires no extra input data and cannot spoil the result, even if the effect is negligible. The linear relations (5) still have a role to play: they facilitate the error analysis and reveal – by comparison with Eqs. (12) – the size of the J -mixing effect.

As an example of use of the proposed algorithm we reconsider the data on Sm-based compounds. The value of H_{ex} deduced from recent magnetic measurements on a single crystal of $\text{Sm}_2\text{Fe}_{17}$, $H_{\text{ex}} = 3.15$ MOe [15], has proved significantly lower than that obtained from the observed intermultiplet transition, $H_{\text{ex}} = 3.8(4)$ MOe [13]. This is clearly outside the uncertainty interval. Hence the need of reconsideration of the INS data treatment carried out in Ref. [13]. Therein Eq. (5.Sm) was used with $\Delta_{\text{so}} = 124$ meV, as taken from Ref. [16]. The so obtained values of H_{ex} are reproduced in the third column of Table 1. Yet, the above value of Δ_{so} was inaccurate —rounded off to 1000 cm^{-1} . Optical data available for Sm insulators suggest $\Delta_{\text{so}} \approx 130$ meV, see Section 4.3 below. A more recent INS study of SmPd_3 found $\Delta_{\text{so}} = 129 \pm 2$ meV [17]. (Later the same authors reported a higher value for SmPd_3 , $\Delta_{\text{so}} = 135 \pm 5$ meV [18], but this is admittedly less accurate.) A similar ‘spin-orbit splitting of about 130 meV’ was observed in SmMn_4Al_8 [19]. Adopting the new value, $\Delta_{\text{so}} = 130$ meV, but still using Eq. (5.Sm), we arrived at the values of H_{ex} given in the fourth column of Table 1. These are shifted systematically downwards by ~ 0.5 MOe with respect to those in the third column. We finally repeated the calculations using $\Delta_{\text{so}} = 130$ meV and Eq. (12.Sm), see the last but one column of Table 1. The allowance for J -mixing has resulted in a further downward shift of H_{ex} by ca. 0.1 MOe (10 T). The latter shift may seem insignificant but we would like to point out that, as far as $\text{Sm}_2\text{Fe}_{17}$ is concerned, the corrected value, $H_{\text{ex}} = 3.3(3)$ MOe, agrees better with that obtained from magnetic measurements, 3.15 MOe [15]. The uncertainty intervals are readily estimated by using Eq. (5.Sm).

Table 1. Intermultiplet transition energies and thence deduced exchange fields on Sm in selected Sm-based magnets.

Compound	E_{inter} (meV)	H_{ex} (MOe)			
		Ref. [13]	Eq. (5.Sm)	Eq. (12.Sm)	CF-corrected
SmCo_5	165.7^a	3.1	2.6	2.6	2.4
$\text{Sm}_2\text{Co}_{17}$	161^b	2.7	2.3	2.2	2.2
$\text{Sm}_2\text{Fe}_{17}$	176 ± 2^c	3.8	3.4	3.3	3.3
$\text{Sm}_2\text{Fe}_{17}\text{N}_3$	163^d	2.9	2.4	2.4	2.2
$\text{Sm}_2\text{Fe}_{14}\text{B}$	179 ± 2^e	4.0	3.6	3.5	3.4
$\text{SmFe}_{11}\text{Ti}$	175.5^f	3.8	3.3	3.3	3.1

^aReference [20].

^bReference [21].

^cAverage of Refs. [22] and [23].

^dReference [23].

^eReference [24].

^fReference [19].

Our final example is the celebrated $\text{Nd}_2\text{Fe}_{14}\text{B}$. The $^4I_{9/2} \rightarrow ^4I_{11/2}$ transition was observed by Loewenhaupt et al. at $E_{\text{inter}} = 282$ meV [25]. For the spin-orbit splitting we take a value of $\Delta_{\text{so}} = 231.4$ meV, deduced in Section 4.1 specifically for $\text{Nd}_2\text{Fe}_{14}\text{B}$. From Eq. (12.Nd) one finds $H_{\text{ex}} = 4.19$ MOe, whereas Eq. (5.Nd) yields 4.22 MOe. Either way, the final result is $H_{\text{ex}} = 4.2(2)$ MOe, for both non-equivalent Nd sites. The J -mixing correction is less than 1%, while the experimental uncertainty amounts to $\sim 5\%$.

Summarising the Section, J -mixing is sometimes worth taking into account but often negligible. In either case, it is a safe and recommended practice to use the corrected equations (12).

3 Is it necessary to allow for crystal field?

3.1 Pr and Nd compounds

We begin by considering systems for which one can give a general negative answer to the above question. Where such a general denial is not possible, like in the case of Sm, a careful case study becomes necessary, taking into consideration local symmetry of the rare earth site and orientation of the exchange field. The main difficulty is that one then needs to know the CF parameters of the system under study – at least some of them and at least approximately.

All of that can be avoided when dealing with permanent-magnet materials containing Pr and/or Nd. Like in the previous section, we shall first demonstrate this statement for Pr and then extend it to Nd.

Let us write down the CF contribution to E_{inter} for Pr, limiting ourselves to just the leading CF term and the first order in perturbation theory:

$$E_{\text{CF}} = J(2J - 1)\alpha_J \Big|_{J=4}^{J=5} A_2^0 \langle r^2 \rangle = (45\alpha_5 - 28\alpha_4)A_2^0 \langle r^2 \rangle = -0.0117 A_2^0 \langle r^2 \rangle \quad (13.\text{Pr})$$

Here α_J is the Stevens factor of the multiplet with a quantum number J , as given by a formula derived following the prescription of Judd [26]:

$$\alpha_J = -\frac{J^2(J+1)^2 + 15J(J+1) + 756}{45J(J+1)(2J-1)(2J+3)} \quad (14.\text{Pr})$$

Relevant to our calculation are the 'usual', or ground-state Stevens factor, $\alpha_4 = -52/2475$, and the one pertaining to the first excited multiplet, $\alpha_5 = -1/75$. The prefactors of α_J in Eq. (13.Pr) are expectation values of the Stevens operator, $O_2^0 = 3J_z^2 - J(J+1)$, for the $|JM\rangle$ states having $M = J$. Finally, A_2^0 and $\langle r^2 \rangle$ are the leading CF parameter and the radial expectation value for the $4f$ electrons [27]. Our goal is to estimate the upper bound of E_{CF} . Therefore, we choose a well-studied permanent-magnet material $\text{Pr}_2\text{Fe}_{14}\text{B}$ – a much higher A_2^0 is unlikely in a metallic system. A convenient compilation of CF data on $\text{R}_2\text{Fe}_{14}\text{B}$ from several sources can be found in Ref. [11]. Taking the higher one of the two values available for $\text{R}=\text{Pr}$, $A_2^0 \langle r^2 \rangle = 31$ meV, we find from Eq. (13.Pr), $E_{\text{CF}} = -0.36$ meV. This correction should be added to the right-hand side of Eq. (7). Alternatively, E_{CF} can be deducted from the total E_{inter} on the left of Eq. (7), in order to keep the right-hand side unaffected by the CF. The latter is equivalent to subtracting E_{CF} from the parenthesis in Eq. (5.Pr). As a result, H_{ex} would increase by as little as 0.03 MOe (3 T), which can be safely neglected.

The neglect is even more justified for Nd compounds, where the CF contribution to E_{inter} is smaller,

$$E_{\text{CF}} = 5.0 \times 10^{-3} \times A_2^0 \langle r^2 \rangle \quad (13.\text{Nd})$$

Taking the highest one of the three values cited for $\text{Nd}_2\text{Fe}_{14}\text{B}$ in Ref. [11], $A_2^0 \langle r^2 \rangle = 32$ meV, we find $E_{\text{CF}} = 0.16$ meV. Deducting this from the parenthesis in Eq. (5.Nd) would reduce H_{ex} by mere 13 kOe (1.3 T). This is truly negligible (0.34%).

In résumé, the CF can be generally neglected when deducing H_{ex} from E_{inter} . This is not to say that the $4f$ energy levels are little affected by the CF. Thus, the CF shifts the final state of the intermultiplet transition in $\text{Pr}_2\text{Fe}_{14}\text{B}$ by $45\alpha_5 A_2^0 \langle r^2 \rangle = -\frac{3}{5} A_2^0 \langle r^2 \rangle \approx -18$ meV. However, the initial state is shifted by roughly the same amount and so the energy difference remains nearly unchanged.

3.2 Sm compounds

No general conclusion can be made *a priori* – compounds have to be studied on a case-by-case basis. Here we shall consider three representative examples:

- $\text{Sm}_2\text{Fe}_{17}$ – CF is negligible;
- $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ – second-order CF correction is necessary;
- $\text{SmFe}_{11}\text{Ti}$ – second- and sixth-order CF corrections are necessary.

As input data in the first case we take the anisotropy constant measured on a single crystal of $\text{Sm}_2\text{Fe}_{17}$ at $T = 5$ K: $K_1 = -660$ J/kg, i.e. -99.2 K/f.u. [15]. This should be contrasted with the low-temperature anisotropy constant of a single crystal of Y_2Fe_{17} , $K_1 = -50.4$ K/f.u. [28]. The difference, -49 K/f.u., is to be attributed to the two Sm atoms in the formula unit of $\text{Sm}_2\text{Fe}_{17}$ and equated to $-\frac{26}{21} A_2^0 \langle r^2 \rangle$, according to the linear single-ion model in the limit of $T \rightarrow 0$ [29]. Hence $A_2^0 \langle r^2 \rangle = 40$ K, or 3.4 meV. Higher-order CF terms are neglected in this rough estimate; our goal is to demonstrate the weakness of the anisotropy rather than to apportion it among the different orders. The expression for the CF contribution to E_{inter} is taken from an earlier paper [13],

$$E_{\text{CF}} = -0.0660 A_2^0 \langle r^2 \rangle - 0.235 A_4^0 \langle r^4 \rangle + 0.192 A_6^0 \langle r^6 \rangle \quad (13.\text{Sm})$$

Prior to being set in this equation, the above value of the leading CF parameter should be multiplied by -0.45, which results in $A_2^0 \langle r^2 \rangle = -1.53$ meV. The transformation of the CF is necessary because the quantisation axis in Eq. (13.Sm) – as well as in all previous equations – is determined by the exchange field \mathbf{H}_{ex} , parallel to the magnetisation vector. In

$\text{Sm}_2\text{Fe}_{17}$, however, the magnetisation direction is distinct from the 3-fold symmetry axis. At low temperature the angle between both directions is about 80° [15], hence the need to multiply by $\frac{3}{2}\cos^2\theta - \frac{1}{2} \approx -0.45$. With $A_2^0\langle r^2 \rangle = -1.53$ meV and $A_4^0 = A_6^0 = 0$, Eq. (13.Sm) yields $E_{\text{CF}} = 0.10$ meV. Deducting this from the parenthesis in Eq. (5.Sm) would reduce H_{ex} by about 7 kOe, or 0.2%. The CF effect in $\text{Sm}_2\text{Fe}_{17}$ is thus negligible.

We now turn to $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. This is a permanent-magnet material endowed with a very large A_2^0 ($A_2^0\langle r^2 \rangle = -28$ meV [30]) – the higher-order CF parameters can be neglected in comparison. By Eq. (13.Sm), the CF correction is $E_{\text{CF}} = 1.8$ meV and, by Eq. (5.Sm), H_{ex} should be reduced by 0.13 MOe. This is worth taking into account. In such a case it is immaterial whether E_{CF} is first deducted from the observed E_{inter} and then the corrected E_{inter} is set in Eq. (12.Sm) or, alternatively, Eq. (12.Sm) is applied first and then $\frac{63}{148}E_{\text{CF}}$ is deducted from the result, the prefactor being that from Eq. (5.Sm). Either way, the final result is 2.2(3) MOe, as given in the last column of Table 1.

Our final example, $\text{SmFe}_{11}\text{Ti}$, is peculiar in having two essentially nonzero CF parameters, $A_2^0\langle r^2 \rangle = -9.5$ meV and $A_6^0\langle r^6 \rangle = 6.0$ meV, while the remaining CF parameters are negligible [31]. By Eq. (13.Sm), one has $E_{\text{CF}} = 1.8$ meV. Unusually, two-thirds of this amount comes from the large sixth-order term, which is manifest in the presence of an inflection point in the magnetisation curve. By Eq. (5.Sm), H_{ex} should be reduced by 0.13 MOe, which results in $H_{\text{ex}} = 3.1(3)$ MOe.

Calculations for the remaining Sm compounds proceed along the same lines. The corrected values of H_{ex} are displayed in the last column of Table 1.

We conclude that for most Sm compounds it is worthwhile to allow for the CF – if the latter is known. If not, one can do without and raise the error margin slightly – the CF correction is never too big.

4 To what extent is Δ_{so} independent of host lattice?

4.1 R = Nd

So far it was tacitly assumed that the intermultiplet splitting in the absence of exchange and CF, Δ_{so} , depends only on the kind of lanthanide R, but not on the lattice hosting it. It is clear that this assumption cannot be generally true. Two ionic compounds of the same lanthanide can be as distinct as Eu_2O_3 and EuO , where Eu^{3+} has $\Delta_{\text{so}} = 43$ meV [16], while Eu^{2+} cannot be reasonably assigned any Δ_{so} since it has $L = 0$. Even if we leave aside such extreme cases and limit ourselves to standard-model, trivalent lanthanides having exactly $Z - 57$ localised electrons in the $4f$ shell, the above question does make sense as Δ_{so} may feel the presence of other, non- $4f$ electrons involved in the chemical bond. For a quantitative answer, we turn to spectroscopic data for non-magnetic ($H_{\text{ex}} = 0$) dielectric (optically transparent) compounds. These data are particularly extensive for $\text{R}=\text{Nd}$, since such materials are interesting for laser applications.

It should be remarked that Δ_{so} is not directly observable in optical experiments. Even in the absence of an exchange field the multiplets of Nd^{3+} are split by an a priori unknown crystal field. To avoid confusion, let us define Δ_{so} to be the energy gap between the barycenters of the ground J -multiplet, $^4I_{9/2}$, and the first excited one, $^4I_{11/2}$. Likewise, Δ'_{so} is defined as the gap between the barycenters of $^4I_{11/2}$ and $^4I_{13/2}$ etc. The determination of Δ_{so} thus necessitates the observation and correct identification of all Stark components of both $^4I_{9/2}$ and $^4I_{11/2}$ (in general, 5 and 6 Kramers doublets, respectively), which presents a true experimental challenge. To find Δ'_{so} , one needs the barycenter of $^4I_{13/2}$, i.e. the positions of 7 more Kramers doublets.

It should be appreciated that spectroscopic experiments are not focused on the correct determination of Δ_{so} or Δ'_{so} . Rather, they aim at finding and identifying as many multiplets as possible, or at least those essential for the operation of lasers. Detailed information on the Stark components of low-lying multiplets is merely a by-product of such experiments; it is often revised in subsequent publications and should be regarded as tentative rather than definitive.

Table 2 presents information on Nd-containing systems where only Δ_{so} could be determined, $^4I_{13/2}$ being not (fully) observed. One can appreciate that in two-thirds of all cases the reported value of Δ_{so} lies in a narrow interval,

$$\Delta_{\text{so}} = 233 \pm 1 \text{ meV.} \quad (15)$$

We believe these to be correct. The remaining one-third, collected in the bottom part of Table 1, are deemed to be mistaken, as will be justified below. A shift of several millielectronvolts may arise when an extraneous spectral line is mistaken for a $4f - 4f$ electronic transition, while the true line remains undetected or ignored.

Table 2. Inter-barycenter splitting Δ_{so} in selected Nd compounds.

Compound	Δ_{so} (meV)	Reference
Nd:La ₂ O ₂ S	233.5	[32]
Nd:Bi ₄ Ge ₃ O ₁₂	232.3	[33]
Nd:BaGd ₂ (MoO ₄) ₄	233.0	[34]
Nd:LaSc ₃ (BO ₃) ₄	232.5	[35]
Nd:Y ₂ SiO ₅ , site II	233.0	[36]
Nd:Lu ₂ SiO ₅ , site II	232.3	ibid.
Nd:Na ₅ La(MoO ₄) ₄	232.2	[37]
Nd:Ba ₂ ZnGe ₂ O ₇ , A1-center	233.6	[38]
Nd:Ba ₂ ZnGe ₂ O ₇ , C-center	233.6	ibid.
Nd:Sr ₅ (PO ₄) ₃ F	232.9	[39]
Nd:CeF ₃	236.4	[40]
Nd:LaVO ₄	234.1	[41]
Nd ₃ Ga ₅ O ₁₂	236.3	[42]
Nd:Lu ₃ Al ₅ O ₁₂	237.5	[43]
Nd:Lu ₃ Ga ₅ O ₁₂	236.4 ^R	[44]
Nd:BaLaGa ₃ O ₇	231.0	[45]

^R Revised data used [46]

Note that Δ_{so} of Nd:Lu₃Ga₅O₁₂ has been deduced from the data presented in Kaminskii's book [46], whereas those of his original work [44] would yield a slightly lower value, $\Delta_{so} = 235.8$ meV, which is still too high. We regard this as an instance of conscious revision of own data, correcting a mistake known to the author. The value is marked with a superscript ^R (*Revised* data used); the original article is referred to within the body of the Table, the book is cited in the footnote.

A more recent publication does not necessarily present an improvement on an earlier one. Thus, for Nd:Sr₅(PO₄)₃F we chose to use the data of a 1994 paper [39] rather than a 1996 one [85]. These are contradicting publications of different authors, only the correct one is cited. The mistake in Ref. [85] was to include an extraneous energy level in ⁴I_{11/2} at 2340 cm⁻¹, while missing a true one between 2470 and 2541 cm⁻¹; the result is $\Delta_{so} = 229.2$ meV, far too low.

Finally, apparent misprints are commented in the footnotes of the tables and the corresponding values are marked either ^O (*Original* data used, the misprint being in one of the books [46,42]) or ^C (*Corrected* data used, the misprint is in the original publication).

Of course, the tentative criterion of correctness (15) needs a justification. With this end in view, we carried out scalar-relativistic electronic structure calculations for structurally ordered Nd compounds, see Table 3. Some of the stoichiometric-looking systems, such as Nd₂S₃ or K₅Nd(MoO₄)₄ are in fact structurally disordered, so they are not included. The details of the calculations are described in the Appendix. The target quantity was the splitting between the 4*f* orbitals of Nd having $j = 5/2$ and $7/2$, Δ_{4f} , which serves as a one-electron measure of intensity of the spin-orbit interaction within the 4*f* shell. Therefore, Δ_{so} must be proportional to Δ_{4f} . By Eq. (7.3) of Ref. [48] combined with the Landé interval rule, one has for Nd³⁺:

$$\Delta_{so} = \frac{11}{21} \Delta_{4f}. \quad (16)$$

This relation is valid in the Russel-Saunders approximation. According to Section 6.5 of Ref. [12], the multiplets ⁴I_{9/2} and ⁴I_{11/2} of Nd³⁺ are, respectively, 97% and 99% pure. Therefore, one may expect the proportionality relation (16) to hold, but with a proportionality factor that is a few per cent off the Russel-Saunders value $\frac{11}{21}$. Now, our calculations summarised in Table 3 demonstrate that Δ_{4f} of different Nd compounds deviate from each other by no more than 2.8 meV. By the proportionality of Δ_{so} and Δ_{4f} , Eq. (15) must hold.

Table 3. One-electron spin-orbit splitting Δ_{4f} in stoichiometric Nd compounds.

Compound	Δ_{4f} (meV)	structural data
Nd (both sites)	456.6	[49]
NdAl ₂	455.1	[50]
NdPd ₃	456.0	[51]
NdIn ₃	455.4	[52]
NdSn ₃	455.4	[53]
NdCl ₃	457.8	[54]
NdAlO ₃	456.0	[55]
NdP ₅ O ₁₄	457.5	[56]
Nd ₂ Fe ₁₄ B (both Nd sites)	454.8	[57]
Nd ₃ Ga ₅ O ₁₂	455.0	[58]
LiNdP ₄ O ₁₂	456.9	[59]
KNdP ₄ O ₁₂	457.3	[60]
NdAl ₃ (BO ₃) ₄	456.2	[61]
NdGaGe ₂ O ₇	456.3	[62]

Let us now turn to the main body of data on Nd systems, where we were able to deduce both Δ_{so} and Δ'_{so} . These data are presented in Tables 4-7. If one first looks at Δ_{so} and ignores Δ'_{so} , the trend established above is confirmed: for about two-thirds of the investigated systems one was able to find correct Δ_{so} values, satisfying the condition (15), while the other one-third of the published spectra contain mistakes.

One gets more insight in the matter by considering Δ_{so} and Δ'_{so} jointly. It turns out that all available data can be divided in 5 groups.

1. Fully correct data sets, such that Δ_{so} obeys Eq. (15), while Δ'_{so} satisfies the following criterion:

$$\Delta'_{\text{so}} = 245 \pm 1 \text{ meV.} \quad (17)$$

This implies that all Stark components of the three lowest multiplets ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$) have been determined correctly. These data are presented in Table 4.

2. Data sets consisting of a correct Δ_{so} and a mistaken Δ'_{so} , see Table 5. The mistake should be sought in the second excited multiplet, $^4I_{13/2}$.

3. Data sets containing a mistaken Δ_{so} and a correct Δ'_{so} , Table 6. The error must be in the ground multiplet, $^4I_{9/2}$.

4. Data sets where both Δ_{so} and Δ'_{so} are wrong, but their sum fulfills a condition,

$$\Delta_{\text{so}} + \Delta'_{\text{so}} = 478 \pm 2 \text{ meV,} \quad (18)$$

which is a sum of Eqs. (15) and (17). There must be a mistake in $^4I_{11/2}$. Such data are listed in Table 6 together with the previous group. The reason is the presence of several intermediate cases satisfying both conditions (17) and (18) but not (15).

5. Finally, there are doubly wrong data sets, see Table 7. At least two multiplets must have been misplaced.

Table 4. Nd data satisfying both conditions (15) and (17).

Compound	Δ_{so} (meV)	Δ'_{so} (meV)	Reference
NdP ₅ O ₁₄	233.0	245.5	[63]
K ₅ Nd(MoO ₄) ₄	233.3	245.3	[64]
Nd:PbMoO ₄	233.5	245.4	[65]
Nd:YVO ₄	232.9	244.7	[66]
Nd:LaCl ₃	233.3	245.7	[67]
Nd:La ₂ Be ₂ O ₅	233.6	245.2	[68]
Nd:Ca(NbO ₃) ₂	233.2	245.3 ^R	[69]
Nd:LaNbO ₄	233.5	245.7	[70]
LiNdP ₄ O ₁₂	232.3	245.7	[71]
Nd:KY(WO ₄) ₂	232.5	245.7	[72]
Nd:KGd(WO ₄) ₂	232.8	245.2	[73]
Nd:KLu(WO ₄) ₂	232.4	244.9	ibid.
NdAl ₃ (BO ₃) ₄	232.0	246.0	[74]
Nd:LiKYF ₅	233.4	245.1	[75]
Nd:LiKGdF ₅ , A-center	233.6	245.9	[76]
Nd:LiKGdF ₅ , B-center	232.5	245.8	ibid.
Nd:NaYGeO ₄	233.3	244.5	[77]
Nd:NaGdGeO ₄	233.1	245.2 ^O	[78]
Nd:GdVO ₄	232.1	245.0	[39]
Nd:Sr ₅ (VO ₄) ₃ F	232.5	244.6	[79]
Nd:Sc ₂ SiO ₅ , site I	233.6	244.2	[36]
Nd:Y ₂ SiO ₅ , site I	232.5	244.6	ibid.
Nd:Lu ₂ SiO ₅ , site I	232.7	244.1	ibid.
Nd:Sc ₂ Si ₂ O ₇	233.4	244.8	ibid.
Nd:Y ₂ Si ₂ O ₇	232.1	244.8	ibid.
Nd:Lu ₂ Si ₂ O ₇	233.0	244.6	ibid.

^R Revised data used [46]^O Misprint in Ref.[42] (⁴*I*_{13/2}): 4364 should read 4316**Table 5.** Nd data satisfying Eq. (15) but not Eq. (17).

Compound	Δ_{so} (meV)	Δ'_{so} (meV)	Reference
Nd:YF ₃	233.5 [†]	246.6 [†]	[80,81]
Nd:LiNbO ₃	233.6	241.5	[82]
Nd:Y ₂ O ₃	233.0	243.8	[83]
Nd:YScO ₃	233.8	243.7 ^C	[84]
Nd:Ca ₅ (PO ₄) ₃ F	232.8	241.8	[85]
Nd:KY ₃ F ₁₀	233.3 ^O	250.3 ^O	[86]
KNdP ₄ O ₁₂	232.5	248.9	[87]
Nd:KY(MoO ₄) ₂	232.2	237.8 ^R	[88]
Nd:NaBi(MoO ₄) ₂	232.7	242.5	[89]
Nd:NaBi(WO ₄) ₂	232.8	243.4	ibid.
Nd:CaAl ₄ O ₇ , site I	232.7	239.6	[90]

[†] ⁴*I*_{11/2} and ⁴*I*_{13/2} as in Ref. [80], ⁴*I*_{9/2} as in Ref. [81].^C Data of the Russian original used (a level at 4354 cm⁻¹ missing in the translation [84]).^O Misprint in Ref. [42] (⁴*I*_{11/2}): 2017 should read 2047.^R Revised data used [46].

Table 6. Nd data fulfilling Eqs. (17) and/or (18) but not Eq. (15).

Compound	Δ_{so} (meV)	Δ'_{so} (meV)	Reference
NdAlO ₃	237.4	245.7	[91]
NdGaGe ₂ O ₇ ($T = 77$ K)	234.1	245.8	[104]
Nd ₂ S ₃	227.2	249.7	[125]
Nd:CaMoO ₄	234.8	241.8 ^O	[93]
Nd:BaY ₂ F ₈	235.3	245.6	[94]
Nd:AlN	224.6	246.0	[95]
Nd:LuTaO ₄	235.7	245.7	[96]
Nd:GdNbO ₄	234.5	243.3	[97]
Nd:YNbO ₄	234.8	244.6	[98]
Nd:LiYF ₄	234.3	245.2	[99]
Nd:LaF ₃	235.8	241.9	[100]
Nd:YAlO ₃	236.4	245.4	[101]
Nd:Y ₃ Al ₅ O ₁₂	237.3	244.7	[102]
Nd:CsLa(WO ₄) ₂	234.6	243.1	[103]
Nd:LaGaGe ₂ O ₇	234.3	246.0	[104]
Nd:LaAlGe ₂ O ₇	234.8	245.5	ibid.
Nd:GdGaGe ₂ O ₇	234.1	245.9	ibid.
Nd:Gd ₃ Sc ₂ Ga ₃ O ₁₂	235.8	245.2	[105]
Nd:Gd ₃ Ga ₅ O ₁₂	236.8	245.5 ^R	[106]
Nd:LuAlO ₃	236.3	244.9	[107]
Nd:Ca ₃ Ga ₂ Ge ₄ O ₁₄	234.3	242.7	[108]
Nd:Sr ₃ Ga ₂ Ge ₄ O ₁₄	236.3	241.8	ibid.
Nd:Ba ₃ LaNb ₃ O ₁₂	235.1	243.3	[109]
Nd:Ba ₃ LaTa ₃ O ₁₂	235.1	242.3	[110]

^O Misprint in Ref. [42] (⁴ $I_{11/2}$): 1892 should read 1982.

^R Revised data used [46].

Table 7. Nd data fulfilling none of the conditions (15), (17) or (18).

Compound	Δ_{so} (meV)	Δ'_{so} (meV)	Reference
Nd:GaN	226.6	243.9	[111]
Nd:LaBGeO ₅	234.7	246.4	[112]
Nd:Y ₃ Sc ₂ Al ₃ O ₁₂	236.9	239.0	[113]

What speaks in favour of our interpretation of the correctness, is the fact that the list of fully correct data (Table 4) is the longest of all, whereas the list of doubly wrong published spectra (Table 7) contains only three items. Potentially, this number can be even reduced to two: the authors of Ref. [113] knew that their level #16 at 4057 cm⁻¹ was incorrect and excluded it from the fit. Their calculation predicted a very different position for that level, 4411 cm⁻¹. If a change from 4057 to 4411 cm⁻¹ was accepted, Δ'_{so} would acquire a correct value of 245.3 meV and the case would be moved to Category 3.

As an alternative explanation of the spectroscopic data one could think of a very strong crystal field, making the multiplets repel each other. However, such a hypothesis would be unable to explain the strange selectivity of the repulsion, leaving either Δ_{so} or Δ'_{so} or perhaps $\Delta_{\text{so}} + \Delta'_{\text{so}}$ unaffected. In most cases the correctness of the spectrum can be restored by shifting a single Kramers doublet, which makes us suspect human error rather than a physical cause.

The most serious argument supporting the criterion (15) is the proportionality of Δ_{so} and Δ_{4f} . For demonstration nine structurally ordered Nd compounds – all insulators listed in Table 3 – were put to a test. Five of them have correct Δ_{so} , satisfying Eq. (15). All five were found to obey the relation

$$\Delta_{\text{so}} = 0.5088 \Delta_{4f} \quad (19)$$

to ± 0.3 meV, see Figure 4. The points pertaining to the other four tested compounds lie far above the line, outside the range of the plot. The quantity ± 0.3 meV corresponds to a typical experimental error in the determination of

inter-barycenter splittings, although a certain CF contribution cannot be excluded. Thus, in Ref. [34] the uncertainty in the positions of individual Kramers doublets is estimated to be ± 0.5 meV (± 4 cm $^{-1}$). This estimate presents the upper bound, valid for the broadest lines; most lines are however much sharper than that. Similar values are given in Ref. [114], albeit for Dy $^{3+}$ rather than Nd $^{3+}$.

We deliberately avoided the extension of spectroscopic Δ_{so} of Nd-doped systems to stoichiometric Nd compounds. The only exception is NdCl $_3$, whose Δ_{so} used in Figure 4 was in fact deduced from the data measured on Nd:LaCl $_3$ [67], cf. Table 4. Such extrapolation is based on an observation [115] that barycenters of lanthanide multiplets do not move under isostructural substitution. Without sufficient first-hand experience in the matter we prefer not to rely on this approximation.

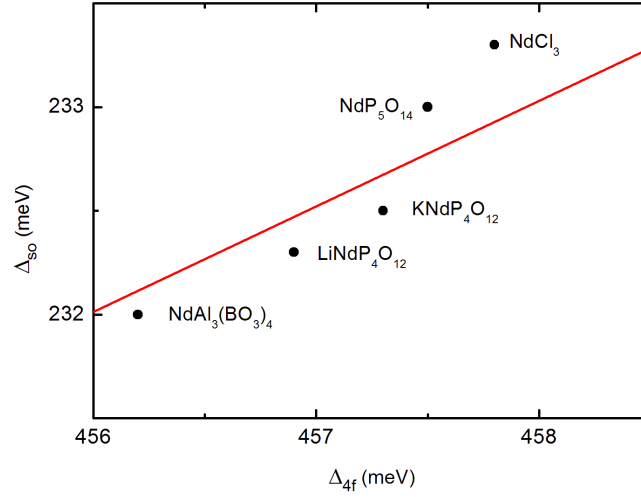


Fig. 4. Inter-barycenter energy gap Δ_{so} deduced from spectroscopic data for selected Nd compounds, plotted against calculated one-electron spin-orbit splitting Δ_{4f} (Table 3). The ordinate of the point labelled 'NdCl $_3$ ' was determined on a doped system, Nd:LaCl $_3$ [67].

We thus arrive at a new correctness criterion for Δ_{so} of Nd systems, Eq. (19), to replace the old one, Eq. (15). The new criterion is physically more appealing but necessitates large-scale calculations. The factor of proportionality in Eq. (19) is 3% lower than the Russel-Saunders value, $\frac{11}{21}$.

To answer the question posed in the title of this section, strictly speaking, Δ_{so} is compound-dependent. A 4-digit value can be found from Eq. (19), which requires a prior calculation of Δ_{4f} for the compound of interest. Taking Δ_{4f} from Table 3, one predicts in particular $\Delta_{so} = 232.3$ meV for Nd metal (both sites), 231.4 meV for Nd $_2$ Fe $_{14}$ B (both Nd sites), 231.5 meV for Nd $_3$ Ga $_5$ O $_{12}$, and 232.0 meV for NdAlO $_3$. For the latter compound this leads to a further prediction that the hitherto unobserved top Kramers doublet of $^4I_{9/2}$ should lie about 810 cm $^{-1}$ (100 meV) above the ground state, as sketched in Figure 5. We have presumed the correctness of all Stark levels observed in Ref. [91] but not the assertion that the level at 595 cm $^{-1}$ is an unresolved quartet, for it has never been seen split into four in a magnetic field.

With somewhat less precision Δ_{so} can be regarded as independent of host lattice. In this case $\Delta_{so} = 232.5 \pm 1.5$ meV should be valid for any Nd compound. For metallic systems it is appropriate to take $\Delta_{so} = 232 \pm 1$ meV.

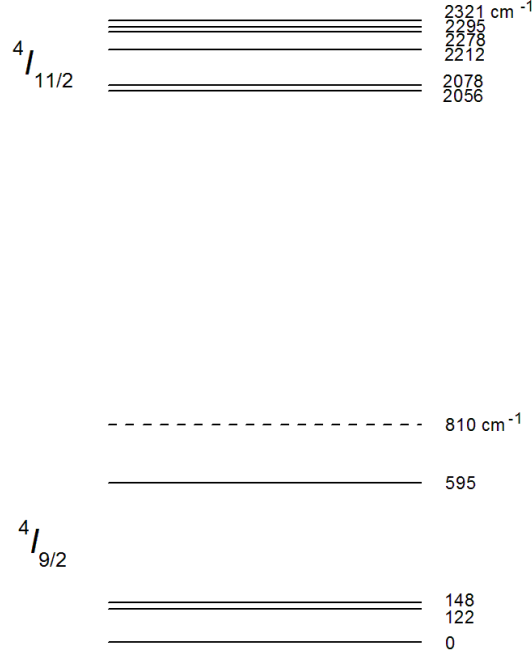


Fig. 5. Energy level diagram of the ground and first excited multiplets of Nd^{3+} in NdAlO_3 . Solid lines: Ref. [91], dashed line: this work (prediction).

4.2 R = Pr

There are few reliable optical data on Δ_{so} in Pr^{3+} , for an obvious reason that it is a non-Kramers ion and so many more Stark components need to be observed and identified. Thus, the determination of Δ_{so} alone necessitates the correct location of 20 levels. The determination of Δ_{so} and Δ'_{so} requires as many as 33 levels. This is a formiddable experimental task. The few sufficiently complete spectra available (see Table 8) should be regarded as tentative. Half of them can be weeded out on a simple criterion that Δ'_{so} should be about 4% greater than Δ_{so} , like in the free Pr^{3+} ion [12]. This is not the 20% required by the Landé interval rule, yet clearly $\Delta'_{\text{so}} > \Delta_{\text{so}}$. Now, all the data sets for PrF_3 and Pr:LaF_3 are to be discarded since they have $\Delta_{\text{so}} > \Delta'_{\text{so}}$. Those for Pr:LaCl_3 and $\text{Pr:K}_2\text{LaCl}_5$ should be retained since they have Δ'_{so} respectively 3% and 5% higher than Δ_{so} . Perhaps, the data for Pr:YAlO_3 and Pr:LaBr_3 should be kept as well.

Table 8. Spectroscopic data for Pr systems.

Compound	Δ_{so} (meV)	Δ'_{so} (meV)	Reference
Pr:LaCl ₃	262.8	271.2	[116]
Pr:LaBr ₃	261.2	n.a.	[117], [12]
Pr:LaF ₃	268.2	260.5	[118]
	264.8 ^A	n.a.	[119]
	277.0	246.6	[120] (Table 1)
	272.7	250.9	[120] (Table 3)
PrF ₃	269.0	255.7	[120], [121] (³ H ₅)
Pr:YAlO ₃	255.4	n.a.	[122]
	259.4	n.a.	[123]
Pr:K ₂ LaCl ₅	257.4	270.3	[124]

^A Assuming a doublet at 2179 cm⁻¹, cf. Table 3 of Ref. [120].

One should add to this that the higher crystal symmetry of PrCl₃ and PrBr₃ enabled a complete and independent determination of CF levels within ³H₄ by means of low-energy INS [3], excluding the top level |0⟩, forbidden for magnetodipole transitions from the ground and first and second excited states. The INS study [3] has fully confirmed, inasmuch as ³H₄ is concerned, the optical results of Ref. [116] for Pr:LaCl₃, but disagreed with those of Ref. [117] for Pr:LaBr₃.

To conclude, optical data suggest a Δ_{so} of about 260 meV. The same value was found in PrAl₂ by means of high-energy INS at room temperature [5].

4.3 R = Sm

Sm-based materials have never been regarded as promising for laser applications, so they are less researched spectroscopically. The few data sets that we managed to extract from the literature (Table 9) are suggestive of a Δ_{so} close to 130 meV.

Table 9. Spectroscopic data for Sm systems.

Compound	Δ_{so} (meV)	Δ'_{so} (meV)	Reference
Sm ₂ S ₃	129.0	143.8	[125]
Sm:LaCl ₃	129.5	150.0	[12]
Sm:LaF ₃	126.0	160.7	[12]
	133.1	149.8	[126]
	131.4	149.8	[127]
Sm:TbF ₃	131.9	n.a.	[128]
Sm:Y ₃ Al ₅ O ₁₂	139.9	148.6	[129, 130]
Sm:Y ₃ Ga ₅ O ₁₂	138.8	147.5	[130]

5 Last but not least: Sample quality does matter

This paper is not about the experimental technique of INS – many important technical questions are left out. So we shall not discuss factors determining instrumental resolution, the choice of incident energy and scattering wave vector, or the role played by temperature. But then we would like to touch upon an issue not particularly revered by neutron spectroscopists – sample quality. Permanent magnet materials are capricious in this respect, to the extent that insufficient sample quality may well make an INS experiment fail. Suffice it to mention Nd₂Fe₁₄B, where a vague transition was observed by Loewenhaupt et al. at $E_{\text{inter}} = 282$ meV [25], not to be seen ever again.

A graphical impression of the role of sample quality can be gained from Figure 6, showing INS spectra of $\text{Sm}_2\text{Fe}_{17}$ from two different sources. The conditions of both experiments were rather similar: same temperature ($T = 20$ K), same equipment, same local contact, somewhat different incident energies (500 meV [131] vs. 350 meV [23]), the two teams had several members in common. What was radically different in those two experiments was the provenance of the samples. And here is the result: two very different spectra. In the lower curve one sees a poorly discernible peak of irregular shape. The upper curve has a prominent absorption line of nearly perfect Gaussian shape (cf. Figure 3 of Ref. [131]). Moreover, a shoulder situated at 130 meV in the upper spectrum indicates the presence of non-magnetic Sm-containing impurities. The less regular shape of the shoulder, clearly visible upon subtraction of the sloping background in Figure 3 of Ref. [131], suggests that several Sm-rich secondary phases may be present. The quality of the lower spectrum permits no judgement in this respect.

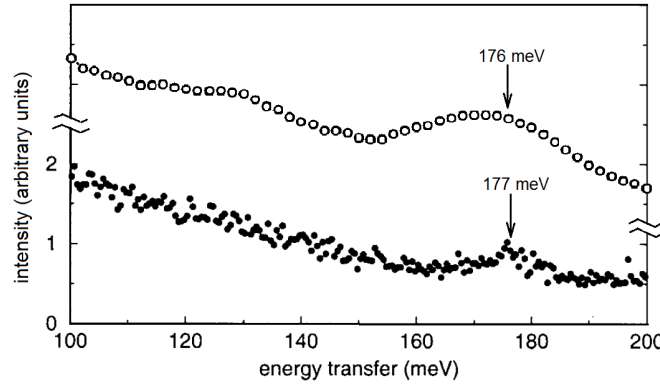


Fig. 6. INS spectra of $\text{Sm}_2\text{Fe}_{17}$ from Refs. [131] (upper curve) and [23] (lower curve).

The cause of the difficulties is two-fold. Firstly, the Sm-Fe phase diagram is such that the $\text{Sm}_2\text{Fe}_{17}$ phase is unstable at high temperature and does not form from the melt. That is to say, an as-cast ingot of stoichiometry 2:17 contains no $\text{Sm}_2\text{Fe}_{17}$ phase at all. Prolonged annealing at a suitably chosen temperature is necessary to make $\text{Sm}_2\text{Fe}_{17}$ form. Solid-state diffusion is a slow process and the result is never perfect. The presence of secondary phases is inevitable. (Much of what we say here applies to $\text{Nd}_2\text{Fe}_{14}\text{B}$ as well [132], but for simplicity of the argument we limit ourselves to the binary R_2Fe_{17} .) From the standpoint of permanent-magnet properties, the main damage comes from inclusions of free iron (α -Fe), which should be avoided at all cost. This is achieved by making the composition slightly off-stoichiometric, richer in rare earth, e.g., R_2Fe_{14} rather than R_2Fe_{17} . The result is the presence of R-rich secondary phases, which are harmless (sometimes even beneficial) as far as the permanent-magnet properties are concerned. They are however detrimental to the spectroscopic properties of these materials.

Secondly, R_2Fe_{17} – as well as other permanent-magnet materials – are rich in iron and poor in rare earth. Conditions for the spectroscopy that only sees rare earth atoms are unfavorable from the outset. The presence of R-rich impurity phases makes the matters worse. For example, suppose there is a single secondary phase – pure rare earth metal making 14.5 at.% of the total ($9 \times \text{R}_2\text{Fe}_{17} + 29 \text{ R}$). The sample is 85.5%-pure R_2Fe_{17} , yet most rare earth atoms (63%) are in the impurity phase. In a more realistic situation there would be several R-rich impurity phases. In a lucky case all of them would be paramagnetic and produce a single secondary peak at $E_{\text{inter}} = \Delta_{\text{so}}$, like in Figure 6 (upper) [131]. In a less favorable case the phases may be magnetically ordered with various H_{ex} , which results in a number of broad, overlapping peaks impossible to interpret.

The remedy is to avoid – inasmuch as possible – the presence of R-rich impurities in spectroscopic samples. By contrast, α -iron can be tolerated. The starting composition should be purposefully shifted towards the iron-rich end.

6 Conclusion

The prospects look good for the use of neutron spectroscopy of intermultiplet transitions for the determination of model parameters of permanent magnet materials, first and foremost, the exchange field on the rare earth H_{ex} . The difficulties of observation and interpretation of the spin-orbit intermultiplet transitions are not insurmountable. To begin with, given the current level of accuracy of determining the transition energies, ± 2 meV, one has an option of simply using Eqs. (5) and regarding Δ_{so} as an atomic constant. More accurate input data would necessitate a more refined treatment. Three effects could become relevant: (I) J -mixing, (II) crystal field, and (III) chemical shift, i.e., dependence of Δ_{so} on the chemical environment of the rare earth atom.

(I) J -mixing can be readily taken into account in general form. No additional input data or preliminary analysis of importance are necessary. It suffices to use improved expressions for H_{ex} (12). The size of the effect becomes apparent a posteriori, by comparison with the uncorrected Eq. (5).

(II) The need of CF correction can be generally ruled out for $R=\text{Pr}$ and, with even more reason, for $R=\text{Nd}$. As against that, the CF correction is usually worthwhile for $R=\text{Sm}$. If the CF is unknown it may be neglected anyway – at the expense of a longer error bar on H_{ex} .

(III) Chemical shift lends itself to quantitative analysis only in the case of $R=\text{Nd}$, owing to the abundance of experimental optical data. The effect proves rather weak and can be often neglected. Thus, for any intermetallic compound of Nd one can take $\Delta_{\text{so}} = 232 \pm 1$ meV, which is sufficient for the treatment of currently available INS data (E_{inter} accurate to ± 2 meV). A more precise prediction of Δ_{so} is possible by way of DFT calculations. For an archetypal permanent-magnet material $\text{Nd}_2\text{Fe}_{14}\text{B}$ the calculations yield $\Delta_{\text{so}} = 231.4$ meV, for both Nd sites.

Interestingly, in the case of $\text{Nd}_2\text{Fe}_{14}\text{B}$ one can neglect both the crystal field and the J -mixing and use the simplest formula (5.Nd) to find H_{ex} . The real problem is to confirm the presence of an intermultiplet transition in $\text{Nd}_2\text{Fe}_{14}\text{B}$, of which only a brief mention exists [25]. The task is not an easy one – we are aware of at least one unsuccessful attempt in the past. In this respect, more attention should be paid to sample preparation. One should realise that recipes for better coercivity are not the same as those aimed at better spectroscopic properties. Impurities that can or cannot be tolerated are distinct in the two cases. In particular, samples destined for the observation of electronic transitions within the $4f$ shell should contain possibly little lanthanide outside the principal phase. In contrast, the presence of α -iron is not unacceptable.

The newly gained ideas about the true values of Δ_{so} and Δ'_{so} should add to the toolbox of techniques for interpreting and debugging Nd spectra, particularly in stoichiometric compounds (NdAlO_3 , NdVO_4 , $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ etc.), where the conventional techniques have failed. It would also be of interest (but outside the scope of this work) to extend this analysis to Δ''_{so} – the gap between the barycenters of $^4I_{13/2}$ and $^4I_{15/2}$.

Acknowledgements

Illuminating discussions with Dr. Klaus Koepnik are gratefully acknowledged.

The irreproachable performance of the computational environment at IFW Dresden as well as the friendly and efficient support of the system administrator were essential for the success of this work. We wish to express our sincere gratitude to Ulrike Nitzsche for both.

Appendix: Computational details

All calculations for the determination of Δ_{4f} in Nd metal and several Nd compounds were performed in the framework of density functional theory. We used the full-potential local-orbital (FPLO) code [133], version FPLO-21.00-61 [134]. This code solves the Kohn-Sham equations for periodic lattices but also permits the calculation of free atoms and ions.

We applied the generalized gradient approximation (GGA) with the parameterization of the exchange and correlation energy functional according to Perdew, Burke, and Ernzerhof (PBE) [136]. In order to account for the non-covalent character of the $4f$ states of Nd, we used the so-called open-core (OC) approach [137]. In this approach the $4f$ orbitals are treated as non-hybridizing core-like states. Their total occupation number was fixed to three in the present case of trivalent Nd. All calculations were performed in non-magnetic mode, which implies identical occupations in both spin channels and corresponds to $H_{\text{ex}} = 0$. Also all $4f$ orbitals are equally occupied in the OC approach, resulting in a spherical $4f$ charge density.

Upon convergence to a self-consistent solution, net occupation numbers of the Nd valence orbitals are obtained. We used the default setting with $5spdf$, $6spd$, and $7s$ orbitals. Their net occupation numbers were used in the further course to define the electron density and, thus, the spin-orbit splitting of the $4f$ states as described below. For the size of the net occupation numbers and the derived electron density, spin-orbit coupling is of minor importance, at least in the case of the considered medium-heavy elements [135]. Thus, FPLO was employed in its default scalar-relativistic mode at this stage.

Integration in reciprocal space was carried out by a linear tetrahedron method on a mesh constructed on the Bravais vectors divided by suitably chosen integers. Those integers as well as the number of atoms per irreducible unit cell are listed in Table 10.

Table 10. Subdivision of the first Brillouin zone for integration in \mathbf{k} -space and number of atoms per irreducible unit cell for all considered Nd compounds.

Compound	\mathbf{k} -mesh	atoms/cell
Nd	$15 \times 15 \times 15$	4
NdAl ₂	$13 \times 13 \times 13$	6
NdPd ₃	$15 \times 15 \times 15$	4
NdIn ₃	$15 \times 15 \times 15$	4
NdSn ₃	$15 \times 15 \times 15$	4
NdCl ₃	$12 \times 12 \times 12$	8
NdAlO ₃	$11 \times 11 \times 11$	10
NdP ₅ O ₁₄	$6 \times 6 \times 4$	80
Nd ₂ Fe ₁₄ B	$6 \times 6 \times 5$	68
Nd ₃ Ga ₅ O ₁₂	$5 \times 5 \times 5$	80
LiNdP ₄ O ₁₂	$7 \times 7 \times 7$	36
KNdP ₄ O ₁₂	$7 \times 7 \times 7$	36
NdAl ₃ (BO ₃) ₄	$8 \times 8 \times 4$	40
NdGaGe ₂ O ₇	$7 \times 7 \times 5$	44

The code DIRAC-21.00-61, which is part of the FPLO package, was used for relativistic calculations solving the four-component Kohn-Sham-Dirac equations for free Nd ions. This was done with fixed orbital occupation numbers that were obtained in the previous calculations for periodic Nd-containing crystals. In this way, the spin-orbit splitting of the $4f$ states was evaluated in an ionic potential that accounts for the system-specific net charge density around the Nd site. Overlap contributions to the charge density were disregarded, since they are mainly localized in the interstitial region. Thus, they do not significantly contribute to the potential gradient experienced by the $4f$ states, which is the source of spin-orbit splitting Δ_{4f} .

Data Availability Statement:

The authors declare that the data supporting the findings of this study are available within the paper.

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