Experimental report

01/10/2023

Proposal: 1-10-50 **Council:** 4/2021

Title: Accurate neutron scattering lengths of Sm- and Nd-isotopes

Research area: Physics

This proposal is a new proposal

Main proposer: Florian GEHLHAAR

Experimental team: Thomas HANSEN
Henry FISCHER
Florian GEHLHAAR

Local contacts: Thomas HANSEN
Henry FISCHER

Samples: NdN
154SmN
152SmN
148SmN
147SmN
SmN
142NdN
143NdN
144NdN
145NdN
146NdN
150NdN
148NdN

Instrument	Requested days	Allocated days	From	To
D20	2	0		
D4	3	8	13/09/2021 24/06/2023	20/09/2021 26/06/2023

Abstract:

The bound coherent neutron scattering length, bcoh(j), is a basic property of an isotope j. Accurate bcoh(j) values are needed in many areas of neutron science. e. g. condensed matter research and nuclear physics. Tabulated scattering lengths have sometimes low accuracy/precision (> 5% error) and / or rely on a single
measurement only. The scope of this proposal is to make use of neutron powder diffraction in order to get both precise and accurate neutron scattering lengths values for some isotopes of samarium (147Sm, 148Sm, 152Sm and 154Sm) and for the seven natural occurring isotopes of neodymium. Both elements are part of many functional materials.
The advantage of Bragg diffraction is that determination relies on relative reflection intensities without the need to normalize to an absolute scale. The
packing density of samples, exact dimensions or weight; important parameters for other techniques of bcoh(j) determination - do not play any role either.
To exclude systematic errors in the diffraction data used for Rietveld refinements on one hand and check wavelength dependency on the other hand, each sample will be measured on two different instruments.

Experimental report on experiment 1-10-50

Accurate neutron scattering lengths of Sm and Nd isotopes

Florian Gehlhaar, Holger Kohlmann (Inorganic Chemistry, Leipzig University, Germany), Henry Fischer, Thomas Hansen (Institut Laue-Langevin, France)

Objectives

The bound coherent neutron scattering lengths, $b_{coh}(j)$, are one of the basic properties of any isotope *j* and many experimental neutron techniques in condensed matter as well as in nuclear physics rely on accurate values. Some of the reported scattering lengths in the widely used collections of scattering lengths [1, 2, 3] have rather low accuracy (> 5% error) and / or rely on a single measurement only and thus clearly need redetermination.

In this experiment the bound coherent neutron scattering lengths b_{coh} of the Nd isotopes ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd, ^{150}Nd and the Sm istopes ^{147}Sm, ^{148}Sm, ^{150}Sm, ^{152}Sm and ^{154}Sm as well as their natural mixtures ^{nat}Nd and ^{nat}Sm were investigated using neutron Bragg diffraction at ambient temperature on polycrystalline powders of binary and ternary compounds containing these isotopes. Extraction of the b_{coh} values is based on kinematic scattering theory applying the Rietveld method was by using the computer programs FullProf[4] and GSAS-II[5] in comparison.

This experiment, together with the previous experiments 1-10-46 and 1-10-48, is part of a project is part of a PhD project to determine neutron scattering lengths.

Experimental Details

Measurements were performed on the high-intensity hot neutron diffractometer D4 at ambient temperature using neutrons with wavelengths of $\lambda = 70$ and 50 pm. Thin-walled vanadium cylinders of 5 mm inner diameter were used as sample containers, being mounted in an evacuated vessel to avoid neutron scattering by air. A polycrystalline nickel sample was used to determine the accurate neutron wavelengths and the instruments profile function.

In order to be able to obtain information about incoherent parts of scattering as well, data were collected for an empty container, the empty vessel and ^{10}B as a strong absorber and packing fraction of samples have been determined by sample mass and container fill hight.

Typical acquisition times were 1-3 hours for large and medium sized samples e.g. sample mass > 100 mg, small or absorbing have been measured several hours and/or overnight.

Since the ^{143}Nd sample turned out to be of natural Nd composition and could not be replaced immediately, additional beam time have been granted in cycle 232 to repeat the measurement. Thanks to the trouble-free performance of the other measurements beam time in both cycles could also be used to investigate additional isotopes, in particular ^{6}Li, ^{7}Li, ^{nat}Li, $^{141=nat}$Pr, ^{nat}Eu, ^{114}Cd, ^{nat}Cd, ^{25}Mg, ^{nat}Mg and ^{123}Te.

Preliminary results and Discussion

Rietveld refinement was performed based on neutron powder diffraction data of the samples, summarized in table 1, with FullProf[4] on the one hand and GSAS-II[5] on the other hand, using appropriate crystal structure models. All parameters (i.e. scale, cell, shape, asymmetry, background, position and temperature factors) were refined simultaneously. All datasets were background subtracted in advance using a linear combination of empty can and empty vessel data. Remaining background was then fitted with a twelfth-degree Chebyshev polynomial function. Since scattering lengths $b_{coh}(j)$ could not be refined directly in either software, the $b_{coh}(j)$ values were obtained via refinement of the site occupation factors for the isotope of investigation and multiplying the results with the corresponding programs internal b_{coh} values. Where possible the isotopes have been investigated in different chemical compounds having different crystal structures to check consistency. Using binary or ternary compounds ensures the independence of absolute intensities, but values will rely on the accurate knowledge of the counter ions while we have chosen Elements such as N, Cl, O, F for this purpose.

Table 1: Bound coherent neutron scattering lengths, $b_{coh}(j)$, all values in fm, as extracted from Rietveld refinement using GSAS-II (GS)[5] and FullProf (FP)[4] for two wavelengths and literature values.
"---" → Measurement not done. "N/A" → Analysis not done yet. "x.xx(e)" → Value with estimated standard deviation given by the programms, grey values from former experiment 1-10-48. All values are already corrected for isotopic enrichment determined by mass spectrometry.

Sample	$b_{coh}(j)$ [1]	$b_{coh}(j)$ [2]	$b_{coh}(j)$ [3]	λ = 50 pm		λ = 70 pm	
				FP	*GS*	*FP*	*GS*
^{142}NdOCl	7.7(3)	7.7(3)	7.7(3)	7.23(7)	n/a	7.18(5)	7.25(5)
^{143}NdOCl	no entry	14(2)	17(1)	17.5(1)	17.5(1)	---	---
^{144}NdOCl	2.8(3)	2.8(3)	2.8(3)	3.09(7)	n/a	2.98(3)	3.02(3)
^{145}NdOCl	no entry	14(2)	8.6(4)	10.31(8)	n/a	10.54(6)	10.46(5)
^{146}NdOCl	8.7(2)	8.7(2)	8.7(2)	8.65(6)	n/a	8.44(6)	8.61(7)
^{148}NdOCl	no entry	5.7(3)	5.8(4)	4.54(7)	n/a	4.43(3)	4.49(3)
^{150}NdOCl	5.28(2)	5.3(2)	5.28(20)	6.86(11)	n/a	6.82(6)	6.86(6)
^{nat}NdN	7.80(7)	7.69(5)	7.72(5)	7.72(10)	7.73(10)	7.82(10)	7.87(10)
^{nat}NdCl$_3$				7.73(5)	7.78(4)	7.85(5)	7.94(4)
^{nat}NdOCl				7.95(5)	n/a	7.66(5)	7.68(5)
^{147}SmN	no entry	14(3)	6.1(6)	6.90(6)	6.76(5)	6.87(6)	6.85(6)
^{147}SmCl$_3$				6.61(5)	6.62(4)	6.62(4)	6.65(4)
^{147}SmOCl				6.63(6)	n/a	---	---
^{148}SmN	no entry	-3(4)	5.9(4)	6.77(5)	6.71(5)	6.74(7)	6.61(8)
^{148}SmCl$_3$				6.70(5)	6.69(5)	6.52(4)	6.36(6)
^{148}SmOCl				6.73(6)	n/a	---	---
^{150}SmN	no entry	14(3)	12.1(2.9)	9.1(8)	9.3(3)	9.2(3)	8.8(3)
^{150}SmCl$_3$				9.91(6)	9.82(6)	10.05(6)	10.00(7)
^{150}SmOBr				10.18(8)	n/a	---	---
^{152}SmN	-5.0(6)	-5.0(6)	-5.0(6)	-6,06(5)	-5.95(4)	-5.72(5)	-5.72(5)
^{152}SmCl$_3$				-6.44(4)	-6.34(4)	-6.17(4)	-6.27(5)
^{152}SmOCl				-6.17(4)	n/a	---	---
^{154}SmN	9.25(1.00)	9.3(1.0)	9.25(1.00)	9.4(3)	9.2(7)	9.2(3)	9.1(6)
^{154}SmCl$_3$				9.43(12)	9.36(9)	9.42(8)	9.26(10)
^{154}SmOBr				9.45(16)	n/a	---	---
^{nat}SmN	0.7(2)-1.5(1)i	0.80(2)-1.65(2)i	0.00(5)	5.27(3)	5.23(3)	7.81(20)	7.86(21)
^{nat}SmCl$_3$				5.23(4)	5.23(4)	7.95(7)	7.77(8)
^{nat}SmOCl				5.26(4)	n/a	---	---
^{141}PrN	4.58(5)	4.58(5)	4.58(5)	4.45(2)	4.44(2)	4.40(2)	4.43(2)
^{141}PrCl$_3$				4.36(3)	4.40(3)	4.45(3)	4.49(3)
^{141}PrOCl				4.43(3)	4.45(3)	---	---
^{nat}EuCl$_3$	5.3(3)	7.22(2)-1.26(1)i	5.3(3)	---	---	5.88(7)	5.92(7)
^{nat}EuN				---	---	5.81(6)	5.96(6)
^{25}MgO	3.62(14)	3.62(14)	3.62(14)	3.73(2)	3.70(2)	3.72(2)	3.72(2)
^{nat}MgO	5.376(20)	5.375(4)	5.376(20)	5.3(1)	5.3(1)	5.27(9)	5.3(1)
^{114}CdF$_2$	7.5(1)	7.5(1)	7.48(5)	5.89(3)	5.88(2)	5.78(3)	5.78(2)
^{nat}CdF$_2$	3.8-1.2i	4.87(5)-0.70i	3.7-1,5i	7.9(8)	8.0(8)	---	---
^{6}LiF	2.0(1)-0.26	2.00(11)-0.261(1)i	2.2(1)	2.27(2)	2.24(1)	2.26(2)	2.25(1)
^{7}LiF	-2.22(2)	-2.22(2)	-2.22(2)	-2.27(2)	-2.28(2)	-2.28(2)	-2.28(2)
^{nat}LiF	-1.90(3)	-1.90(2)	-1.95(3)	-1.98(2)	-1.95(1)	-1.95(2)	-1.95(2)

All seven naturally occurring neodymium isotopes were studied in this experiment in the chemical form of NdOCl, as shown in Table 1. The natural isotope mixture was also measured in the compounds $NdCl_3$ and NdN. Their scattering length does not seem to be unambiguously determined, as can be seen from the different entries in the three given tables. Unfortunately, with our results varying as well we cannot clearly confirm or decline one of these values. The average over all our results is 7.8 fm with a standard deviation of about 0.1 fm. It can be seen that precision for more complex structures of $NdCl_3$ and NdOCl is higher than for high-symmetric NdN, since the scattering length od ^{nat}Nd is similar to the one of ^{nat}N causing a high correlation to the scale factor and thus making the determination more dependent on absolute intensities than on relative ones.

The results for the individual isotopes are largely consistent for different wavelengths and the different programs. Values for ^{143}Nd and ^{145}Nd have not been determined experimentally yet, but just estimated using the other values. Since the isotope samples are not 100% enriched, even the experimental determination of the individual neutron scattering lengths also depends on all others. The values shown in Table 1

were calculated using a 7x7 matrix taking into account the isotope analysis. Since ^{143}Nd could only be measured at 50 pm, our results for 70 pm are accordingly not completely independent. The resulting calculated scattering length for ^{nat}Nd is 7.78(5) fm for λ = 70 pm using FullProf and 7.84(6) fm using GSAS. For λ = 50 pm only analysis with FullProf was carried out so far, the resulting value is 7.86(8). The results are quite comparable within their uncertainties and in good agreement with our direct measurements of ^{nat}Nd samples.

The knowledge about the scattering lengths of the seven natural occurring samarium isotopes is even more unsatisfying than for neodymium. However, they are also more difficult to determine since ^{144}Sm is quite rare, and thus expensive, and ^{149}Sm is one the strongest neutron absorbers and therefore not only difficult to measure but scattering length is also highly-dependent on the neutron energy. Again, we have studied different compounds at different neutron wavelengths and not found the values always as consistent as for neodymium. To ensure the matrix to be fully determined for $b_{coh}(^{iso}Sm)$ calculation, we used $b_{coh}(^{144}Sm)$ = 4.63(4) fm given by Mughabab[3] and $b_{coh}(^{149}Sm)$ = 14 fm and 31 fm for λ = 50 pm and λ = 50 pm, respectively, taken from energy-dependent data given by Lynn et al.[6]. SmN is definitely not a suitable compound to investigate the scattering lenghs of ^{150}Sm and ^{154}Sm since their values seem to be very close to those of ^{nat}N and thus causing a high-correlation with the scale factor as mentioned before and can be seen by the high uncertainties given in table 1. Moreover, the scattering lengths of ^{148}Sm and ^{150}Sm seem to be affected by the energy dependence of b_{coh} of ^{149}Sm which accounts for a share of over one percent in the two samples. However, in very good agreement are the results for $b_{coh}(^{nat}Sm)$ = 5.23(4) fm at λ = 50 pm, we clearly suggest this wavelength to for investigations of samarium containing compounds, if the crystal structures allows such short wavelengths.

Values for $b_{coh}(^{141}Pr)$ are in good agreement for different compounds as well as for different neutron wavelengths. The average of values obtained in this experiment is 4.43 fm with a standard deviation of 0.04 fm and thus about 3 % lower than the often-tabulated value of 4.58 fm. It is actually more close to the value of 4.45 fm also mentioned in the table of Koester and Rauch[1]. As expectable, the estimated standard deviations obtained from the refinements are slightly lower using PrN as a probe, than using the more complex $PrCl_3$ or PrOCl, since the scattering lengths of ^{141}Pr and ^{nat}N (9.36(2) fm)[2] are different by about a factor of two and thus uncertainties are not affected by bad scattering contrast as described before.

Europium in natural isotopic composition has only been measured at an incident neutron wavelength of 70 pm, since its high-absorbing isotope ^{151}Eu has a local minimum in absorption cross-section around the corresponding neutron energy of 168 meV, making it the wavelength/energy of choice to measure europium containing samples[7]. However, b_{coh} values of ^{nat}Eu are strongly energy dependent in the thermal region and thus difficult to determine accurately. From the measurements executed in this experiment we obtain values around 5.9 fm, slightly higher than the value listed for this neutron energy of 5.6 fm by Lynn et al.[6]

^{25}Mg was measured since the tabulated scattering length was suspected to be not accurate. Indeed, we found a value about 3% higher than previous one providing a better precision as well. The new values has already been published[8]. ^{nat}Mg has just been measured for comparison. The precision which can be obtained by using ^{nat}MgO is limited strongly due the similarity of the corresponding b_{coh} values as described before.

^{114}Cd is an isotope often used to avoid high-absorbing ^{113}Cd in neutron scattering experiments and thus its accurate coherent scattering length is quite important. CdF_2 appears to be an excellent compound to reach good precision, since it has hardly any free parameters and $b_{coh}(^{19}F)$ = 5.654(10) fm is well established. Values found by FullProf and GSAS are in good agreement for each neutron wavelength, but differs significantly comparing both wavelengths. This could be due to the influence of remaining 0,7 % ^{113}Cd, whose b_{coh} value is strongly dependent on neutron energy as it is also the case for europium. In addition, the accuracies of all the obtained values are also affected by the accuracy of the other known ^{iso}Cd b_{coh} values since the ^{114}Cd enrichment is just about 98%. However, the value of 7.5 fm which can be found in all the popular references [1, 2, 3] is way too high and clearly cannot be reconciled with our measurements.

^{nat}Li and its isotopes ^{6}Li and ^{7}Li have been investigated in the form LiF forming the rock salt structure type. Values obtained in this experiment and in former measurements at other instruments and wavelengths show a very good reproducibility. A precision between 1.0 and 0.5 % can be reached. The values for ^{6}Li, ^{7}Li and ^{nat}Li appear to be a little higher than tabulated in the other older tables by Koester and Rauch[1], and Sears[2] and are closer to the ones in the newer Atlas of neutron Resonances by Mughabghab [3], as shown in table 1.

Literature

[1] L. Koester, H. Rauch, E. Seymann, *At. Data Nucl. Data Tables* **1991**, *49*, 65–120

[2] V. F. Sears, *Neutron News* **1992**, *3*, 26–37

[3] S. F. Mughabghab, *Atlas of Neutron Resonances. Resonance Properties and Thermal Cross Sections Z= 1-60 = 1-60,* 6. Aufl., Elsevier Science, San Diego, **2018**.

[4] J. Rodriguez-Carvajal, FULLPROF version 7.95, **2023**, ILL unpublished

[5] B. H. Toby, R. B. von Dreele, *J. Appl. Crystallogr.* **2013,** *46*, 544–549

[6] J. E. Lynn, P. A. Seeger, *Atom. Data nucl. Data* **1990**, *44*, 191–207.

[7] J. Lee, J. Hori, K. Nakajima, T. Sano, S. Lee, *Journal of Nuclear Science and Technology* **2017**, *54*, 1046–1057.

[8] H. Mohammadi, R. Da Mendes Silva, A. Zeidler, L. V. D. Gammond, F. Gehlhaar, M. de Oliveira, H. Damasceno, H. Eckert, R. E. Youngman, B. G. Aitken, H. E. Fischer, H. Kohlmann, L. Cormier, C. J. Benmore, P. S. Salmon, *The Journal of chemical physics* **2022**, *157*, 214503.