Subfamilies

If for a polytypic substance the OD family and thus the OD layers are determined, it may occur that the investigation of another sample of the substance yields new maximal ERs. In this case the ERs chosen do not meet all sites of possible disorder, and at least one kind of ERs have to be replaced by new maximal ERs defining new additional limits for OD layers. This leads to a splitting of the original OD layers. Obviously, the structures of the original family are contained in the new family. Any of the new maximal ERs fulfils the conditions for ERs also in the original family.

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Determination of Anomalous Scattering Lengths of Samarium for Thermal Neutrons*

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Abstract

Anomalous scattering lengths of natural Sm for thermal neutrons with wavelengths between 0·827 and 1·300 Å have been determined by single-crystal diffraction from a Sm complex of known structure. 140 selected reflections were measured at a temperature of 37 K at each wavelength and $b_0 + b'$ and b'' refined in each case. The values obtained are in good agreement with values obtained from a Breit–Wigner calculation using tabulated absorption resonance parameters for ^{149}Sm. A value of $b_0 = 4{\cdot}3 \pm 0{\cdot}2$ fm is deduced from the diffraction experiments.

Introduction

Anomalous scattering of thermal neutrons by resonant nuclei has been exploited for crystal-structure determination – see, for example, Bartunik (1978), Flook, Freeman & Scudder (1977), Koetzle & Hamilton (1975), Schoenborn (1975), Sikka & Rajagopal (1975) and references cited therein.

For successful application of phase determination techniques the anomalous scattering lengths must be known at all wavelengths employed in an experiment. We report here the determination of the scattering lengths of natural Sm at a number of wavelengths from measurements of reflections from a single crystal of known structure. The refined values are compared with values calculated from absorption resonance parameters. A preliminary report of this work has been published by Engel & Koetzle (1982).

Table 1 gives a list of references to previous neutron diffraction determinations of scattering lengths of nuclei with large imaginary components.

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Table 1. *Previous reports of neutron diffraction determination of scattering lengths for nuclei with large imaginary components*

Reference	Resonant nucleus	Compound used
Peterson & Smith (1961)	^{113}Cd	CdS
Peterson & Smith (1962)	^{6}Li	$Li_2SO_4.H_2O$ (98%.^{6}Li)
Peterson & Smith (1962)	^{10}B	BP
Smith & Peterson (1964)	^{113}Cd	CdI_2 (natural and 87·3% ^{113}Cd)
McDonald & Sikka (1969)	^{113}Cd	$Cd(NO_3)_2.4D_2O$
Sikka (1969)	^{149}Sm	$Sm(BrO_3)_3.9H_2O$
Koetzle & Hamilton (1975)	^{149}Sm	$NaSmC_{10}H_{12}N_2O_8.8H_2O$
Fuess & Bartunik (1976)	^{113}Cd	$Cd(C_6H_8N_3O_2)_2.2H_2O$

Breit–Wigner calculation of b

The scattering length of natural Sm for thermal neutrons is (notation of Mughabghab & Garber, 1973; Bacon, 1975)

$$b = b_0 + b' + ib'' \tag{1}$$

$$b_0 = \sum \omega_j \left(R'_j - \sum_i \frac{g_i \lambda_{0i}}{4\pi} \frac{\Gamma_{ni}}{E_{0i}} \right) \tag{2}$$

$$b' + ib'' = \frac{g\omega\lambda_0}{4\pi} \frac{\Gamma_n (E - E_0)}{(E - E_0)^2 + (\Gamma/2)^2} + i \frac{g\omega\lambda_0}{4\pi} \frac{\Gamma_n \Gamma/2}{(E - E_0)^2 + (\Gamma/2)^2}. \tag{3}$$

The second and third terms are the dispersion terms for the thermal resonance of the 149 isotope. The first term is the sum of wavelength-independent terms over all other resonances, i, and all isotopes, j, present. For convenience we abbreviate the expression to

$$b = b_0 + \frac{A(E - E_0)}{(E - E_0)^2 + B^2} + i \frac{AB}{(E - E_0)^2 + B^2}. \tag{4}$$

The parameters of (4) can be calculated from the following absorption resonance parameters tabulated in the compilation by Mughabghab & Garber (1973): $2g\Gamma_n = 0{\cdot}600\ (9)$ meV; $\Gamma_\gamma = 60{\cdot}5\ (6)$ meV; $\Gamma_\alpha = 0{\cdot}060\ (25)$ μeV; $E_0 = 0{\cdot}0976\ (3)$ eV [$\lambda_0 = 0{\cdot}916\ (1)$ Å]; $I = 7/2$; $J = 4$ ($g = 9/16$); $\omega = 0{\cdot}138$. The resulting values are listed in the first column (absorption) of Table 4.

The total real scattering length $b_{re} = b_0 + b'$ and b'' calculated from these absorption parameters are plotted as full curves in Fig. 1 using a value of $b_0 = 4{\cdot}3$ fm chosen to obtain the best fit with values determined in the diffraction experiment.

b_0 was also calculated from (2) using published values of E_0 and $2g\Gamma_n$ (Mughabghab & Garber, 1973). The calculation is shown in Table 2. A value of $b_0 = 2{\cdot}80$ fm is obtained for natural Sm.

There are several sources of uncertainty in this value. The values of the potential scattering length R' were taken from an optical model calculation (Fig. 1 on p. xx in Mughabghab & Garber, 1973). R' varies very rapidly between mass numbers 144 and 150 resulting in a high degree of uncertainty in this range. For isotopes 144 and 148 the resonance parameters have not been published. However, the low absorption cross sections of these isotopes for thermal neutrons suggest that their contributions will be very small, of the order of 0·05 fm for isotope 148 and 0·005 fm for 144.

Bound states reported for isotopes 147, 149 and 150 provide large contributions. Any uncertainty or omissions in the published values would thus drastically affect the value obtained for b_0. Further, the expression summed in (2) is an approximation valid

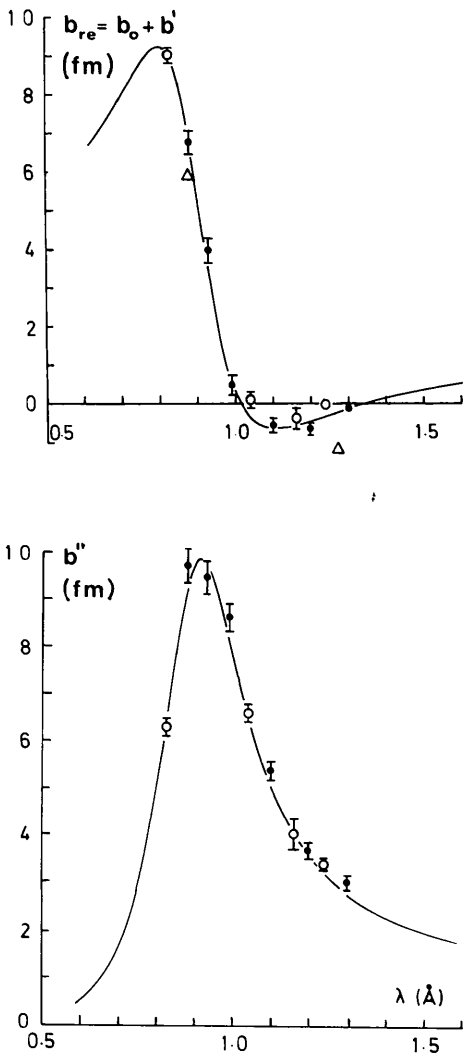

Fig. 1. Real scattering length $b_{re} = b_0 + b'$ and imaginary scattering length b'' of natural Sm plotted against neutron wavelength. Full curves are Breit–Wigner calculations from absorption resonance parameters taking $b_0 = 4{\cdot}3$ fm. Points are values refined from diffraction data. ● Data from crystal at 37 K; ○ data from smaller crystal at room temperature; △ values reported by Sikka (1969).

Table 2. *Calculation of b_0 for natural* Sm *from resonance parameters (all values in* fm)

A is the nuclear mass number of the relevant isotope, σ_γ the radiative capture cross section for thermal neutrons [barns (1 b = 100 fm^2)], ω the isotopic abundance in natural Sm, R' the potential scattering length and S the sum of contributions in (2), the figure in parentheses being the contribution to S of a bound state. The sum S for isotope 149 is over all resonances excluding the thermal resonance with $E_0 = 0{\cdot}0976$ eV.

A	σ_γ	ω	R'	S	$b_0 = R' - S$	ωb_0
144	0·7	0·0309	4·52	—	4·52	0·14
147	64	0·1497	6·2	3·72 (−1·69)	2·48	0·37
148	2·7	0·1124	7·1	—	7·1	0·80
149	41 000	0·1383	7·9	−1·56 (−7·31)	9·46	1·31
150	102	0·0744	8·10	0·36 (−2·82)	7·74	0·58
152	206	0·2672	8·20	15·33	−7·13	−1·91
154	5·5	0·2271	8·15	1·47	6·68	1·52
						2·80

for values of the primary neutron energy E far from any resonance energy E_0. Over the range of values of E used in this experiment ($E = 0{\cdot}05$–$0{\cdot}13$ eV for wavelengths $\lambda = 1{\cdot}3$–$0{\cdot}8$ Å) the values of certain contributions will vary appreciably. For a wavelength of 1 Å ($E = 0{\cdot}082$ eV) the value of b_0 is reduced to 2·56 fm.

Two experimental values of $b_0(a_{coh})$ are available for pure isotopes, namely $-5{\cdot}0 \pm 0{\cdot}6$ fm for 152 (Mughabghab & Garber, 1983) and $9{\cdot}25 \pm 1{\cdot}0$ for 154 (Koehler, 1981). Using these values instead of those in Table 2 increases the value of b_0 from 2·56 to 3·72 fm. In view of the above considerations the calculation of b_0 must be regarded as rather unreliable.

Experimental

A single crystal of a sodium salt of the samarium–edta complex, $Na^+[Sm(C_{10}H_{12}N_2O_8).3H_2O]^-.5H_2O$, was used for the investigation. This compound crystallizes in space group $Fdd2$ with $Z = 16$ and has lattice parameters $a = 19{\cdot}428\,(10)$, $b = 35{\cdot}334\,(15)$, $c = 12{\cdot}014\,(6)$ Å at a temperature of 37 K. The sample was approximately octahedral in shape measuring $4{\cdot}4 \times 1{\cdot}7 \times 2{\cdot}1$ mm along **a**, **b** and **c**, respectively, and was mounted on an aluminium pin sealed in a helium-filled aluminium can. The can was placed in a closed-cycle helium refrigerator,* cooled to 37 K and mounted on an automated four-cycle diffractometer at the Brookhaven high flux beam reactor. The neutron beam was monochromated using the (002) face of a Be crystal. Reflections were measured at a neutron wavelength of 1·300 Å, sampling all accessible Bijvoet pairs out to $\sin\theta/\lambda = 0{\cdot}33$ Å^{-1} and one octant out to $\sin\theta/\lambda = 0{\cdot}54$ Å^{-1}. Intensities were corrected for absorption by means of Gaussian numerical integration (Busing & Levy, 1957). Details of the calculation

* Air Products and Chemicals Inc., Displex® Model CS-202.

Table 3. *Refined values of scattering lengths of natural* Sm

N is the number of independent reflections used. μ is the calculated linear absorption coefficient. The absorption cross section of Sm was calculated from $\sigma_a = 2\lambda b''$ and thence the mass absorption coefficient using $\mu/\rho = \sigma_a N_0/A$, where N_0 is Avogadro's number and A the atomic weight. The absorption cross section for H was calculated using $\mu/\rho = 2{\cdot}39\lambda$ (Å) (m^2 kg^{-1}) assuming hydrogen to be a '$1/v$' scatterer with an atomic absorption cross section of 40 barn (4×10^3 fm^2) at $\lambda = 1$ Å. The contributions due to other atoms were neglected. The density of the crystal was taken as 1·91 g cm^{-3} (Koetzle & Hamilton, 1975). A_{max} and A_{min} are the maximum and minimum values of the transmission factor. The volume of the crystal used was 7·50 mm^3.

λ (Å)	$b_0 + b'$ (fm)	b'' (fm)	N	μ (mm^{-1})	A_{max}	A_{min}
0·827*	9·00 (20)	6·30 (20)	278	2·21	0·259	0·119
0·880	6·76 (31)	9·72 (36)	131	3·26	0·051	0·022
0·930	3·97 (32)	9·47 (37)	130	3·64	0·046	0·018
0·990	0·48 (26)	8·36 (30)	140	3·26	0·052	0·021
1·040*	0·10 (20)	6·60 (20)	276	2·78	0·210	0·081
1·100	−0·55 (19)	5·38 (21)	133	2·33	0·087	0·046
1·160*	−0·37 (27)	4·02 (34)	302	2·01	0·250	0·109
1·198	−0·64 (16)	3·67 (18)	128	1·87	0·130	0·081
1·240*	−0·03 (9)	3·38 (14)	1936	1·75	0·354	0·193
1·300	− 0·00 (5)	2·90 (6)	1795	1·63	0·184	0·095
0·88†	5·9 (8)					
1·27†	−1·2 (4)					

* Values obtained using data measured with a smaller crystal (volume 0·77 mm^3) at room temperature. The measurements at wavelengths 0·827, 1·040 and 1·240 Å were made by Koetzle & Hamilton (1975). Certain values of scattering lengths reported here differ somewhat from theirs owing to the correction of an arithmetic error and do not represent new measurements.
† Values reported by Sikka (1969).

of the linear absorption coefficient are given in the legend to Table 3. The structure was refined to the final unweighted R value based on F^2 of 0·059 for 1795 independent reflections, the refinement being partially anisotropic with 434 parameters including the real and imaginary Sm scattering lengths. The refinement was complicated owing to disorder in the water molecules, and some disordered atoms retained rather high temperature factors. The crystal structure and further experimental details are reported elsewhere (Engel, Takusagawa & Koetzle, 1983).

140 reflections with strong Sm contribution to the structure factor were then selected and measured at a number of additional wavelengths between 0·827 and 1·198 Å. The diffractometer was particularly suitable for this series of measurements as the entire instrument was mounted on an arm which could be rotated to change the monochromator take-off angle. The instrumental resolution was such that $\Delta\lambda/\lambda \sim 0{\cdot}02$. Absorption was severe and reflections consequently weak, particularly close to the resonance. The largest μ value was 3·64 mm^{-1} at $\lambda = 0{\cdot}930$ Å with the minimum calculated transmission of $A = 0{\cdot}018$.

From the structural parameters obtained in the full refinement based on the 1·300 Å data, the real and imaginary scattering lengths of Sm were refined together with the scale factor for each limited data

Table 4. *Parameters of* (3) *and* (4) *for calculating scattering lengths*

Values refined from the diffraction experiment are compared with values deduced from the published absorption data (Mughabghab & Garber, 1973).

	Absorption	Diffraction	
		from b_{re}	from b''
A (fm eV)	0·302 (6)	0·299 (32)	0·310 (23)
B (eV)	0·0305 (3)	0·0310 (24)	0·0310 (12)
E_0 (eV)	0·0976 (3)	0·0966 (11)	0·0972 (8)
b_0 (fm)	(3·7)*	4·32 (21)	—
Γ_n (meV)	0·533 (8)	0·526 (60)	0·546 (41)
Γ (eV)	0·0610 (6)	0·0619 (49)	0·0620 (24)

* Incorporates experimental b_0 values for isotopes 152 and 154.

set obtained at the other wavelengths. The refined scattering lengths are given in Table 3. The values of the scattering lengths used for the other atoms in the crystal (in fm) are $b_{Na} = 3·63$, $b_C = 6·6484$, $b_N = 9·36$, $b_O = 5·803$ and $b_H = -3·7409$ (Koester, 1977).

Discussion

In Fig. 1 the refined scattering lengths can be compared with theoretical curves calculated from the resonance parameters of ^{149}Sm. As mentioned above, the curve of $b_0 + b'$ was drawn using a value of $b_0 = 4·3$ fm chosen to provide a good fit. The agreement between the refined values of the scattering lengths and the theoretical curves is good.

The parameters A, B, E_0 and b_0 of (4) were calculated from the experimental values of b_{re} and b'' by a least-squares refinement using the program *GAUSHAUS* (University of Wisconsin). The refined values are compared in Table 4 with those deduced from the published absorption resonance parameters (Mughabghab & Garber, 1973).

All values are consistent. The e.s.d.'s of values deduced from the absorption resonance parameters (first column) are lower than those of the refined ones, and therefore the former should be used when calculating scattering lengths. However, as pointed out above, the value of b_0 from (2) is most uncertain. It is therefore recommended that for diffraction work the value of $b_0 = 4·3 \pm 0·2$ fm deduced from the present diffraction experiment be used.

Sikka & Rajagopal (1975) give equations similar to (4) and recommend parameters to be used with them. Equivalent values, however, differ quite considerably from those used here.

Finally, we calculate b for pure ^{148}Sm at a standard wavelength of 1 Å. From (4), $b' = -4·04$ fm and $b'' = 7·81$ fm for ^{149}Sm diluted to 13·83% in natural Sm. The value of b_0 for ^{149}Sm is calculated as 7·8 fm at 1 Å rather than 9·46 fm (Table 2). This yields, for pure ^{149}Sm, $b = b_0 + b' + b'' = 8 - 29 + 56i = -21 + 56i$ fm. Bacon (1978) gives the value $b = -19 + 45i$ fm. While the difference in the real part is of doubtful significance the value of 56 for the imaginary part is probably more reliable.

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