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Neutron scattering length determination by means of total scattering

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A new method for the measurement of bound coherent neutron scattering lengths is reported. It is shown that a relative measurement of the neutron scattering length, \overline{b} , of an element can be made by analysis of the neutron correlation function of a suitable oxide crystal powder. For this analysis, it is essential to take into account the average density contribution to the correlation function, as well as the contributions arising from distances between atoms in the crystal. The method is demonstrated and verified by analysis of the neutron correlation function for the corundum form of Al₂O₃, yielding a value \overline{b} = 3.44 (1) fm for Al, in good agreement with the literature. The method is then applied to the isotopes of iridium, for which the values of the scattering lengths were unknown, and which are difficult to investigate by other methods owing to the large cross sections for the absorption of neutrons. The neutron correlation function of a sample of Sr_2IrO_4 enriched in ¹⁹³Ir is used to determine values \overline{b} = 9.71 (18) fm and $\overline{b} = 12.1$ (9) fm for ¹⁹³Ir and ¹⁹¹Ir, respectively, and these are consistent with the tabulated scattering length and cross sections of natural Ir. These values are of potential application for obtaining improved neutron diffraction results on iridates by the use of samples enriched in ¹⁹³Ir, so that the severe absorption problems associated with ¹⁹¹Ir are avoided. Rietveld refinement of the neutron diffraction pattern of isotopically enriched Sr₂IrO₄ is used to yield a similar result for Ir. However, in practice the Rietveld result is shown to be less reliable because of correlation between the parameters of the fit.

1. Introduction

Iridate compounds are of fundamental interest owing to their unique electronic and magnetic behaviours (Crawford et al., 1994; Kim et al., 2008; Fujiyama et al., 2014; Sala et al., 2014; Takayama et al., 2015; Chun et al., 2015), and are of practical interest because of their catalytic properties (Sardar et al., 2011, 2012, 2014). Neutron diffraction (ND) is an important structural probe of these materials, especially their magnetic structures, with the potential to yield accurate and detailed structural information. Nevertheless, ND measurements on samples with a significant Ir content are challenging, owing to the very high absorption cross section of natural iridium ^{Nat}Ir (see Table 1). The neutron absorption cross section of the isotope ¹⁹³Ir is significantly smaller than that of ^{Nat}Ir, and thus samples made with Ir enriched in ¹⁹³Ir have the potential to be advantageous for ND. However, the well known compilations of values for the coherent neutron scattering lengths of stable elements and isotopes (Mughabghab, 1984; Koester et al., 1991; Sears, 1992; Rauch & Waschkowski, 2002) do not include a value for ¹⁹³Ir or ¹⁹¹Ir, and it appears that values have never been reported in the literature. Although the absorption cross section of ¹⁹³Ir is markedly less than that of ^{Nat}Ir, it is still higher than for most elements, and thus the measurement of

The (natural) abundance, the coherent neutron scattering length, \overline{b} , and the coherent, incoherent and total scattering cross sections for natural Ir and its isotopes.

Also given is the absorption cross section for a neutron energy of 25.30 meV and the energy of the nuclear resonance with the lowest energy. The values are taken from Rauch & Waschkowski (2002), except where indicated otherwise.

Element or isotope	Abundance (%)	\overline{b} (fm)	$\sigma_{\rm coh}$ (barn)	$\sigma_{\rm incoh}$ (barn)	$\sigma_{\rm scatt}$ (barn)	$\sigma_{\rm abs}$ (barn)	Lowest resonance energy (meV)
^{Nat} Ir	_	10.6 (3)†	14.1 (8)	0.0 (3.0)	14.0 (3.0)	425 (2)	_
¹⁹¹ Ir	37.3	12.1 (9)‡	_	_	_	954 (10)	652.8 (5.0)§
¹⁹³ Ir	62.7	9.71 (18)‡	_	_	_	111 (5)	1298 (1)§

† The error on this value is quoted in compilations as 0.2 fm (Mughabghab, 1984) or 0.3 fm (Koester *et al.*, 1991; Sears, 1992; Rauch & Waschkowski, 2002), but the original report gives no indication of the experimental error (Mueller *et al.*, 1963). ‡ This work. § Mughabghab (1984).

Table 2The coherent neutron scattering lengths and absorption cross sections(for neutron energy 25.3 meV) of the elements considered in this work(Rauch & Waschkowski, 2002).

Element	\overline{b} (fm)	$\sigma_{\rm abs}$ (barn)	
0	5.805 (4)	0.00019 (2)	
Al	3.449 (5)	0.231 (3)	
Sr	7.02 (2)	1.28 (6)	
^{Nat} Ir	10.6 (3)	425 (2)	

its scattering length is challenging. In this article we report a new method for obtaining a relative measurement of the coherent scattering length, by analysis of the neutron correlation function of a suitable oxide crystal powder, which is able to overcome the difficulties of absorption sufficiently well to provide a reliable measurement. The method is first demonstrated and verified by application to a measurement of the (already known) scattering length of aluminium from the differential correlation function of the corundum form of Al₂O₃. The method is then used to determine the scattering lengths of ¹⁹³Ir and ¹⁹¹Ir from the differential correlation function of a sample of Sr₂IrO₄ enriched in ¹⁹³Ir. Both of the samples studied are oxides, dominated by oxygen (i.e. the oxygen atomic fraction exceeds 50%), and the scattering length of oxygen is well known with a relatively small error (Table 2). Since the method introduced here provides a relative measurement, oxides are well suited to the method.

There have been a few previous reports of total scattering studies on liquids that have revealed errors or inconsistencies in tabulated scattering length values. For example, in ND studies of methanol, Turner *et al.* (1991) concluded that one possible explanation for their results is that the published scattering length value for ¹³C is considerably too low. However, this article is the first report of the use of total scattering to actually measure a scattering length. The method introduced here relies on the atomic structure of the sample being accurately known, and ND measurements on liquids or glasses would not be well suited to the method.

2. Experimental procedures and results

 Al_2O_3 in the corundum form was supplied by Potterycrafts Ltd (P3300, 99.0% calcined alumina). Isotopically enriched Ir (97.6% ¹⁹³Ir), referred to here as ^{iso}Ir, was supplied by Trace

Sciences International. The Sr_2IrO_4 sample was made by reaction of the ^{iso}Ir metal powder with $SrCO_3$ (Alfa Aesar, puratronic 99.994% metals basis). The ^{iso}Ir and dried $SrCO_3$ were thoroughly ground together in an agate mortar and pestle, compressed into pellets and then heated at 1473 K for 30 min in a high-purity alumina boat. This treatment was followed by thorough grinding and a further heating of the repelleted sample at 1473 K for 12 h. This sample is referred to here as isotopically enriched Sr_2IrO_4 .

Prior to the manufacture of the isotopically enriched Sr_2IrO_4 sample, an ND measurement was made on the ^{iso}Ir metal powder [see Fig. S1(*a*) in the supporting information]. Only Bragg peaks due to Ir (Swanson *et al.*, 1955) were observed, indicating that the ^{iso}Ir metal powder was chemically pure. The number density of Ir atoms in pure Ir is about seven times higher than for Sr_2IrO_4 , and consequently the measurement on ^{iso}Ir was much more adversely affected by absorption. Thus, the result for ^{iso}Ir is not discussed in detail, and in fact it is not useful for scattering length determination, as is discussed below. The chemical purity of the ^{iso}Ir was also confirmed by X-ray diffraction (see Fig. S1*b*).

The GEM diffractometer (Hannon, 2005) at the ISIS Facility pulsed neutron source was used to measure the neutron correlation functions of Al₂O₃ and isotopically enriched Sr₂IrO₄ at room temperature. A 3.356 g sample of Al₂O₃ was placed inside a cylindrical container of radius 4.15 mm, made from 40 µm vanadium foil. The isotopically enriched Sr₂IrO₄ sample (1.5337 g) was placed inside a cylindrical vanadium container of inner and outer radius 2.985 and 3.175 mm, respectively. The standard corrections for background, absorption, multiple scattering and inelasticity were made using the Gudrun program (Soper, 2011) and the ATLAS suite of software (Hannon et al., 1990). Statistical errors were propagated throughout the data correction and reduction process. Normalization was achieved using a standard null alloy V-Nb rod of radius 3.975 mm, and data from detector banks 2, 3, 4 and 5 (at mean scattering angles 17.26, 34.04, 61.56 and 91.72°) were combined to yield the corrected experimental distinct scattering, $i_{exp}(Q)$, shown in Fig. 1. Each detector bank provides reliable data over a different range in momentum transfer, Q, and the distinct scattering is obtained by merging of the results from these detector banks so that it covers the wider range shown in the figure. The ND data presented here are available from the ISIS Disordered Materials Database (Hannon, 2013*b*).

For Al₂O₃, the sample was of a larger size, leading to better statistical accuracy, and furthermore only a minor correction for absorption was required (because of its small absorption cross sections, see Table 2); the mean absorption cross section per atom is 0.092 barn. Thus, reliable results were obtained up to a high maximum momentum transfer, Q_{max} , of 50 Å⁻¹.

For isotopically enriched Sr₂IrO₄, the sample was smaller and relatively highly absorbing (absorption cross section per atom is 19.11 barn), leading to poorer statistical accuracy. In addition, owing to the residual amount (2.4%) of ¹⁹¹Ir in the isotopic Ir, the data were affected by the ¹⁹¹Ir nuclear resonance at 652.8 meV (Mughabghab, 1984), and as a consequence the reliable *O* range for each detector bank was more restricted (Hannon, 2015). Thus, the corrected distinct scattering was limited to a more modest Q range for $i_{exp}(Q)$, with a value of 23 Å⁻¹ for Q_{max} . A difficulty with correcting the data for the isotopically enriched Sr₂IrO₄ sample is that the values of σ_{scatt} for the isotopes of Ir are not known and hence the value for ^{Nat}Ir was used to evaluate the corrections. However, the fitting method used to analyse the correlation function includes a normalization factor, and therefore the effect of using this value is negligible. Also, since σ_{incoh} for ^{Nat}Ir is small



Figure 1

The corrected experimental distinct scattering, $i_{exp}(Q)$, for (a) Al₂O₃ and (b) isotopically enriched Sr₂IrO₄ (after subtraction of paramagnetic scattering).

(see Table 1), it is likely that σ_{scatt} for ¹⁹³Ir is similar to the value for ^{Nat}Ir (see below for further discussion of this point), in which case the effect of using the ^{Nat}Ir value on the normalization will be small.

The presence of hydrogenous impurity in a sample can be a severe problem for total scattering measurements [e.g. see Fischer *et al.* (2008)], owing to the large incoherent scattering cross section of hydrogen (Sears, 1992; Rauch & Waschkowski, 2002), combined with its large inelasticity effect, which arises from the similarity of the proton and neutron masses (Soper, 2009). The samples studied here are unlikely to contain hydrogenous impurities, because the Al₂O₃ sample was calcined, whilst the Sr_2IrO_4 sample was prepared at high temperature for a long time, but nevertheless the experimental results were checked for evidence of hydrogen. For time-offlight ND, the presence of hydrogen manifests itself clearly in the measurements in two ways: firstly, as an overall increase in the scattering level due to the large incoherent scattering cross section, and secondly as a high degree of inconsistency in the Q dependence of the intensities (Soper, 2009) measured by detectors at different scattering angles (i.e. different detector banks). No such evidence was observed for either sample, giving a very high degree of confidence that the samples did not contain even a small amount of hydrogenous impurity.

The next section of this article describes how the distinct nuclear scattering, i(Q), measured for a sample can be Fourier transformed to obtain a correlation function in real space. However, for samples containing magnetic ions, there is a magnetic contribution to the scattering in addition to the contribution from the nuclear scattering (Price & Sköld, 1986); the magnetic scattering contribution should be removed prior to the Fourier transformation. If the sample is in the paramagnetic state, then the magnetic scattering is smooth and continuous with a simple dependence on the squared magnetic form factor, and it may be calculated and subtracted (Hannon, 1989). Sr_2IrO_4 is magnetically ordered at low temperature, with an ordering temperature of \sim 250 K, but it behaves as a paramagnet at room temperature with a small Ir⁴⁺ moment of $0.33 \mu_B$ (Kini et al., 2006). The paramagnetic scattering for Sr₂IrO₄ was calculated, using the magnetic form factor parameters for Ir⁴⁺ calculated by Kobayashi et al. (2011), and this was subtracted from our ND data. The calculated paramagnetic scattering is approximately three orders of magnitude smaller than the nuclear scattering, and the effect of this correction was minimal. The magnetic scattering for iridates is extremely small and this makes it very challenging to measure, especially because of the additional difficulty that arises from the very high absorption cross section of natural iridium, ^{Nat}Ir (see Table 1). The measurement of magnetic scattering from iridates is one of the subject areas that may benefit from the use of isotopically enriched Ir, and in particular from the scattering length value reported in this article.

3. Outline of theory

The quantity measured in an ND experiment (Hannon, 1999a,b, 2015) is the differential cross section

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = I^{\mathrm{S}}(Q) + i(Q), \qquad (1)$$

where $\hbar Q$ is the magnitude of the momentum transfer, $I^{s}(Q)$ is the self scattering and i(Q) is the distinct scattering. [The separation of the cross section into self and distinct parts¹ is an alternative and equivalent formalism to a separation into incoherent and coherent parts. Whereas the incoherent/

coherent formalism is more commonly used in the conventional theory for diffraction from crystalline materials, the self/ distinct formalism is more suitable for the theory of total scattering (Hannon, 2015).] The self scattering, which can be calculated approximately, is subtracted from the corrected data to give the distinct scattering. Structural information may then be obtained by a Fourier transformation of i(Q), yielding the differential correlation function [sometimes known as the pair distribution function, PDF (Billinge & Kanatzidis, 2004)]:

$$D(r) = \frac{2}{\pi} \int_{0}^{\infty} Qi(Q)M(Q)\sin(rQ)\,\mathrm{d}Q,\qquad(2)$$

where M(Q) is a modification function introduced to take into account the maximum experimentally attainable momentum transfer, Q_{max} . The differential correlation function, D(r), represents the deviation of the distribution of scattering length from the average density contribution, $T^0(r)$, so that the total correlation function is

$$T(r) = T^{0}(r) + D(r) = 4\pi r g^{0} \langle \overline{b} \rangle_{av}^{2} + D(r), \qquad (3)$$

where $g^0 = N/V$ is the macroscopic atom number density and $\langle \overline{b} \rangle_{av} = \sum_l c_l \overline{b}_l$ is the average coherent neutron scattering length for the sample (the *l* summation is over elements). c_l and \overline{b}_l are, respectively, the atomic fraction and coherent neutron scattering length for element *l*. For the current study, it is of central importance to note that $T^0(r)$ depends on the scattering lengths.

The total correlation function is a weighted sum of partial correlation functions, $t_{ll'}(r)$:

$$T(r) = \sum_{l,l'}^{l \ge l'} c_l (2 - \delta_{ll'}) \overline{b}_l \overline{b}_{l'} t_{ll'}(r), \qquad (4)$$

where the l, l' summations are over all unique pairs of elements in the sample and $\delta_{ll'}$ is the Kronecker delta. An interatomic distance r_{jk} , due to atom pair j and k, with coordination number n_{jk} and RMS (root mean square) variation in distance $\langle u_{jk}^2 \rangle^{1/2}$ contributes a peak to the relevant partial correlation function with the following form:

Table 3

Rietveld refinement results for full refinement in space group $I4_1/acd$ of ND data on isotopic Sr_2IrO_4 , including refinement of Ir site occupancy.

Refined lattice parameters are a = 5.49616 (17), c = 25.7893 (9) Å.

Site	Wyckoff position	Occupancy	x	у	z	$U_{\rm iso} \times 100 ({\rm \AA}^2)$
Sr	16 <i>d</i>	1	0	0.25	0.55059 (2)	0.791 (14)
Ir	8 <i>a</i>	0.9279 (17)	0	0.25	0.375	0.281 (11)
O1	16 <i>d</i>	1	0	0.25	0.45489(2)	0.806 (14)
O2	16 <i>f</i>	1	0.20190 (8)	0.45190 (8)	0.125	0.994 (17)

$$t_{jk}(r) = \frac{n_{jk}}{r_{jk}(2\pi \langle u_{jk}^2 \rangle)^{1/2}} \exp\left[-\frac{(r-r_{jk})^2}{2 \langle u_{jk}^2 \rangle}\right].$$
 (5)

The area, $A_{ll'}$, under the peak in T(r) is then given by

$$A_{ll'} = \frac{n_{jk}(2 - \delta_{ll'})c_l \overline{b}_l \overline{b}_{l'}}{r_{jk}}.$$
 (6)

Thus the value of a particular scattering length affects both the area under relevant peaks in T(r) [or D(r)] and the slope of the average density contribution, $T^0(r)$ [see equation (3)].

In summary, a peak in the correlation function corresponds to a commonly occurring interatomic distance in the sample. Furthermore, the area under the peak depends on the corresponding coordination number, also weighted according to the scattering lengths of the elements involved.

4. Discussion

4.1. Rietveld refinement for Sr₂IrO₄

Rietveld refinement has often been used as a method of scattering length determination (Boucherle & Schweizer, 1975; Koester et al., 1991; Rodriguez et al., 2007; Kennedy & Avdeev, 2011; Kohlmann et al., 2016) and the site occupancy can be refined as a proxy for scattering length in standard Rietveld programs. We performed a Rietveld refinement of the ND data collected on GEM for Sr₂IrO₄ to evaluate the application of this method to the measurement of the scattering length, \overline{b}_{iso} , for ^{iso}Ir. Scale factors, shifted Chebyshev polynomial backgrounds, appropriate diffractometer constants, atomic positions, displacement parameters, absorption corrections and profile parameters were refined using GSAS and EXPGUI (Larson & Von Dreele, 2004; Toby, 2001) for banks 3-6 of GEM, covering the d-spacing range 0.31–7.1 Å (corresponding to a Q range of 20.15–0.89 Å⁻¹). The literature value (10.6 fm, see Table 1) of the scattering length of ^{Nat}Ir was used for these refinements. The site occupancy of Ir was then refined, the refinement smoothly converging to a value of 0.9279 (17), with a weighted profile Rfactor $R_{wp} = 0.0396$ and $\chi^2 = 4.26$ for 61 variables [see results in Table 3 and Fig. 2(a)]. The parameters for this refinement are very similar to those in a previous report for Sr₂IrO₄ (Crawford et al., 1994) and, furthermore, we found no evidence for any impurity or other phase in the sample. Assuming full occupation of the Ir site, the refined occupancy value is equivalent to an ^{iso}Ir scattering length of 9.836 (18) fm and the

¹ The self scattering cross section (Squires, 1978; Price & Sköld, 1986) arises from the interference between the wave scattered by each atom with the wave scattered by itself. The distinct scattering cross section arises from interference between the wave scattered by each atom and the waves scattered by all of the other atoms in the sample, not including itself.

small error bar appears to indicate that a very precise value has been obtained. However, the correlation matrix for the refinement indicates that the occupancy was 51.3% correlated with the isotropic displacement parameter, U_{iso} , of the Ir site. We believe it to be well known that a strong correlation between occupancy and displacement parameters (and, depending on the O range measured, absorption) is a common problem in Rietveld refinement; nevertheless, to our knowledge this is a limitation of the method that has received very little attention in the literature. An exception is the work of Heuer (2001), who said 'Even for refinements with acceptable fits, correlations between the thermal displacement parameters and site-occupancy factors can lead to considerable uncertainties. One refinement may be precise, but the single results from several refinements can scatter in a larger range than suggested by the estimated standard deviations.' Given the high degree of correlation, we have investigated the accuracy of the result by making a series of Rietveld refinements based on the original refinement described above, but using the following two methods to map out the phase space: (i) fixing U_{iso} for the Ir site and refining the occupancy; (ii) fixing the occupancy and refining the Ir U_{iso} . This allowed us to map $R_{\rm wp}$ as a function of $U_{\rm iso}$ and occupancy, the results of which are shown in Fig. 3. It is quite clear that an effectively equivalent refinement quality can be obtained for a large range of occupancy (scattering length) values and therefore



Figure 2

(*a*) Rietveld refinement of ND data on isotopic Sr_2IrO_4 (GEM bank 6, mean scattering angle 154.26°), including refinement of scattering length for ^{iso}Ir (*i.e.* Ir site occupancy). (*b*) Refinement of ND data on isotopic Sr_2IrO_4 using scattering length for ^{iso}Ir determined by fitting the correlation function (GEM bank 6). Red points are experimental data, whilst green and black lines, respectively, show the fit and the residual (displaced).

the small error obtained on the occupancy in the full refinement is misleading. The contour plot in Fig. 3 shows that, in terms of U_{iso} and \overline{b}_{iso} , the minimum in R_{wp} is broad and shallow. The absolute minimum value of R_{wp} is 0.0396 (Table 3), but for example a slight increase in R_{wp} to only 0.0398 can correspond to a change in \overline{b}_{iso} of more than 0.1. Or, to put it another way, the innermost contour in Fig. 3 (for $R_{wp} =$ 0.0398, compared with $R_{wp} = 0.0396$ for the best fit) corresponds to a range in ^{iso}Ir scattering length covering about 9.7– 10.0 fm. In this situation, an alternative method of determining the value of the scattering length is of value.

4.2. Introduction of the method for determination of \overline{b}

In essence, the method introduced here allows the bound coherent neutron scattering length, \overline{b} , of an element to be determined by fitting the differential correlation function, D(r) [see equation (2)], for a crystal powder of known structure. The value of \overline{b} influences the different contributions to D(r) in several ways, and these are demonstrated here by means of simulations of the correlation functions, performed using the XTAL program (Hannon, 1993, 2013a). The simulations calculated by this program include the broadening effects of both thermal motion [see equation (5)] and realspace resolution [arising from the finite value of Q_{max} and the choice of modification function, see equation (2)]. The simulations were calculated using the same values of Q_{max} and the same choices of modification function as used to analyse the experimental data [50 \AA^{-1} and the Lorch function (Lorch, 1969) for Al₂O₃; 23 Å⁻¹ and the step function (Hannon, 2015) for isotopically enriched Sr₂IrO₄].

The simulations for Al_2O_3 (Fig. 4) were calculated using lattice parameters and atomic coordinates taken from a literature report of the crystal structure (Thompson *et al.*, 1987), whilst the simulations for Sr_2IrO_4 (Fig. 5) were





Contour map of R_{wp} for Rietveld refinements of ND data for isotopic Sr_2IrO_4 with various values of the occupancy and isotropic displacement parameter U_{iso} for the Ir site; see text for details. The right-hand axis shows values of \overline{b}_{iso} corresponding to the occupancy values shown on the left-hand axis.

calculated using the parameters given in Table 3. Because of the effect of correlated motion, there is less thermal broadening for short distances in the correlation function (especially between bonded atoms) than for longer distances (Wright & Sinclair, 1985; Jeong *et al.*, 1999, 2003). Therefore the thermal broadening was simulated using the distance-dependent values for the RMS thermal variation in distance, $\langle u_{jk}^2 \rangle^{1/2}$, given in Table 4. The long-range value of $\langle u_{jk}^2 \rangle^{1/2}$ can be determined by conventional crystallographic analysis (*e.g.* Rietveld refinement), but for short distances, $\langle u_{jk}^2 \rangle^{1/2}$ can only be determined reliably from the measured correlation

T(r)







Simulations of the correlation functions for Al₂O₃, calculated with the literature value for \overline{b}_{Al} , unless stated otherwise. (a) The total correlation function (continuous line), $T_{sim}(r)$, together with the average density term (dashed line), $T^0(r)$. (b) The Al–O (blue), O–O (red) and Al–Al (green) contributions to $T_{sim}(r)$. (c) The differential correlation function, $D_{sim}(r)$, calculated with the literature \overline{b}_{Al} value (black), and with the value of \overline{b}_{Al} decreased (blue) and increased (red) by 10% compared with this value.



	Al_2O_3			Sr ₂ IrO ₄		
	Atom pairs	Distance range	$\langle u_{jk}^2 \rangle^{1/2}$ (Å)	Atom pairs	Distance range	$\langle u_{jk}^2 \rangle^{1/2}$ (Å)
Shortest bonds	Al-O	<2.5 Å	0.06	Ir-O	<2.4 Å	0.06
Second shortest bonds	None			Sr-O	2.4–2.65 Å	0.07
Next-nearest neighbours	0-0	2.5–4.0 Å	0.08	0-0	2.65–3.4 Å	0.11
-	Al-Al			Ir-Sr		
				Sr-O		
Long distances	All	>4.0 Å	0.10	All	>3.4 Å	0.13

The thermal broadening factors (RMS variation in distance) used to simulate the correlation functions of Al₂O₃ and Sr₂IrO₄ shown in Figs. 4 and 5.

function itself. The $\langle u_{jk}^2 \rangle^{1/2}$ value, 0.06 Å, in Table 4 for the shortest bonds is typical of experimental results for Al–O bonds (Hannon & Parker, 2000; Barney *et al.*, 2007; Hannon *et al.*, 2008), whilst the longer distance values are approaching the values derived from crystallographic isotropic displacement parameters for both Al₂O₃ (Thompson *et al.*, 1987) and Sr₂IrO₄ (Table 3).

As is apparent in Figs. 4 and 5, the individual peaks in the correlation function at short distance are well separated from each other, but rapidly become overlapping at longer distance, and it is the short distance features that are used for scattering length determination, because this region has the most separation of the different contributions from each other. The area of a peak in T(r) is proportional to the product of the scattering lengths of the two elements involved [see equation (6)] and, for example, the area of an Al-O peak is proportional to $\overline{b}_{Al}\overline{b}_{O}$. Thus for Al₂O₃ the areas of the (Al-Al or Al-O or O-O) peaks are proportional to \overline{b}_{Al}^{-2} or \overline{b}_{Al} , or independent of \overline{b}_{Al} . Consequently, the scaling of the different peaks in the total correlation function, T(r), relative to each other is sensitive to the value of \overline{b}_{AI} , and the best available separation between regions with different dependences on the scattering length of interest is obtained at low r. However, it is the differential correlation function, $D(r) = T(r) - T^{0}(r)$, that is obtained directly from an ND experiment [equation (2)], and the value of D(r) at a particular distance, r, is determined both by the contributions from the peaks due to nearby interatomic distances and by the average density contribution $-T^{0}(r)$. For consideration of the method, it is helpful to divide D(r) into several regions, discussed here in terms of Al₂O₃. The first region of D(r), at low r before the first peak (distances shorter than ~1.6 Å), depends only on $-T^0(r)$ and hence its only dependence on \overline{b}_{Al} is via the average scattering length, $\langle \overline{b} \rangle_{av}$ [see equation (3)]. The second region includes the nearest-neighbour Al-O peak (distances shorter than \sim 2.25 Å), and hence it has a contribution that is proportional to \overline{b}_{Al} , as well as the contribution from $-T^0(r)$. For longer distances, the origins of the features in D(r) are more complex, but at shorter distances it is useful to divide D(r) into regions, where each region is formed of a peak manifold, and each manifold has contributions from a number of peaks which are due to only a small number of different types of structural interaction. The structural description of each individual peak for Al₂O₃ and Sr₂IrO₄ is given in tables later in the article, where the fit results are reported. For Al_2O_3 , the first of these peak manifolds covers the distance range $\sim 2.25-2.89$ Å; there

are both O–O and Al–Al contributions, and the simulations (Fig. 4) show that this region has little sensitivity to \overline{b}_{Al} .

It is important to note that the normalization of the experimental correlation function, $D_{\exp}(r)$ [obtained directly from Fourier transformation of the experimental distinct scattering, $i_{\exp}(Q)$], cannot be relied on to be perfect (Alderman *et al.*, 2014; Hannon, 2015), so that the correctly normalized differential correlation function is given by

$$D(r) = f_{\text{norm}} D_{\text{exp}}(r).$$
⁽⁷⁾

Here, f_{norm} is a normalization factor, which is allowed to vary in the fitting process. The value of f_{norm} deviates from one for a variety of reasons, such as errors in estimating the number of atoms in the neutron beam for a powder, sample-dependent background *etc.* (Alderman *et al.*, 2014). Nevertheless, if the corrections of the experimental data have been performed satisfactorily, the value of f_{norm} should not deviate from one by more than say 10%.

The simulations in Figs. 4 and 5 show the effects on D(r) of 10% variation in the values of \overline{b}_{Al} and \overline{b}_{Ir} , respectively. Clearly, variation in the value of the scattering length of interest, \overline{b} , affects some regions of D(r) much more strongly than others and therefore a good value of \overline{b} can be obtained by fitting a sufficiently wide distance range so that it includes regions with different dependences on \overline{b} . Furthermore, the fit should include the low-*r* region prior to the first peak, which depends solely on $\langle \overline{b} \rangle^2_{av}$ and f_{norm} . Note also that the apparent effect of a change in the value of \overline{b} on a peak in D(r) may be counter-intuitive because of the competing effects of $-T^0(r)$ and the area of the peak itself.

As a result of the introduction of the normalization factor, $f_{\rm norm}$, the method introduced here is essentially a relative method; for example, in the next section we use experimental data for Al₂O₃ to determine the value of \overline{b}_{Al} , but this uses the literature value for \overline{b}_{O} , and the value obtained for \overline{b}_{Al} is thus dependent on the value of \overline{b}_{0} . In principle, the method introduced here could be applied to experimental data for a monatomic sample, and this may seem attractive because then the resultant value of \overline{b} would not be a relative value. However, for a monatomic sample, the area of all correlation function peaks and the slope of $-T^0(r)$ depend on \overline{b}^2 [see equations (3) and (6)], and therefore the value of f_{norm} cannot be refined. Consequently the accuracy of the value of \overline{b} is determined by the initial normalization of the experimental data (typically this is reliable to $\sim 10\%$) and in practice this means that the accuracy is much poorer.

Note that the simulations for Sr_2IrO_4 (Fig. 5) are based on the literature value of the scattering length for natural Ir (Table 1), since the scattering lengths of the two isotopes are not already known.

4.3. Determination of \overline{b} for Al

The corundum form of Al_2O_3 is suitable for demonstrating and verifying the method for several reasons. Its structure is well established, and in particular its local structure has some similarity to Sr₂IrO₄, in that the shortest interatomic distances in both compounds arise from oxygen octahedra. Thus an analysis method developed for Al₂O₃, which gives a reasonable value of \overline{b} for Al, is likely to work well for Sr₂IrO₄ too. Aluminium and oxygen are both commonly studied elements and the scattering length for each natural element is well known with a small error (Rauch & Waschkowski, 2002). However, in the analysis presented here, the value of \overline{b}_{A1} is treated as though it is unknown, so that it may be determined (relative to the value of \overline{b}_{Ω}) by fitting the measured correlation function, and then tested by comparison with the literature value (Table 2). An additional reason for the choice of Al_2O_3 to demonstrate and verify the method is that the crystal structure has one Al site and one O site, so that its local structure, and hence the distribution of short interatomic distances, is not excessively complicated. On the other hand, note that the literature value of \overline{b}_{Al} is small compared with that of \overline{b}_{0} , making it harder to determine accurately.

The experimental corrections for Al₂O₃ are very well behaved, since absorption is slight (see Table 2), and the inelasticity correction is not severe (Hannon, 2015); thus the experimental distinct scattering, $i_{exp}(Q)$, was well determined up to a high momentum transfer (Fig. 1a). Fig. 6 shows the experimental differential correlation function, $D_{exp}(r)$, obtained by Fourier transformation of $i_{exp}(Q)$ for Al₂O₃. For this Fourier transformation, the Lorch modification function (Lorch, 1969) with a maximum momentum transfer, Q_{max} , of 50 \AA^{-1} was used, yielding a high resolution in real space with a full width at half-maximum (FWHM) of 0.109 Å. For values of r less than the shortest interatomic distance in the sample, the differential correlation function, D(r), should ideally be equal to $-T^{0}(r)$, so that it is proportional to r in this region [see equation (3)]. In practice, experimental results, $D_{exp}(r)$, do not perfectly adhere to this behaviour. Firstly, there are Fourier ripples and statistical noise in the experimental result. Secondly, an unphysical error peak is often observed at a short distance in the range below ~ 1 Å, which arises because of imperfections in the experimental corrections. Most corrections change relatively slowly in Q space, compared with the genuine experimental information, and hence inadequacies in the corrections give rise to an error peak at low r. For the Al₂O₃ data shown in Fig. 6, a negative error peak is observed at $r \simeq 0.1$ Å and all fits were performed using a minimum distance, r_{\min} , of 0.50 Å.

Fig. 6(*a*) shows the total function that was fitted to the experimental correlation function, $D_{exp}(r)$, over the distance range from 0.50 to 3.58 Å. This range was chosen to be wide

enough to include contributions with all the different dependences on \overline{b}_{Al} , as discussed in the previous section and illustrated in Fig. 4. The coordination number for each distance was determined from the known crystal structure (Thompson et al., 1987) and was not varied in the fit; it is assumed the structure is fully ordered and in particular that the occupancies of all crystallographic sites are one (this is an essential assumption of the method). The initial values of the interatomic distances were determined from the crystal structure (Thompson et al., 1987), and for Al-Al and O-O atom pairs the values were not varied. On the other hand, the Al-O distances were allowed to vary in the fit, because in oxides it is the cation-oxygen distances that are mainly affected by correlated motion, so that they differ from the interatomic distances determined from the average structure measured by crystallographic methods (Dove et al., 1997); it was found to be necessary to vary the Al-O distances to achieve the extreme closeness of the fit shown in Fig. 6. The thermal widths, $\langle u_{ik}^2 \rangle^{1/2}$, of all the peaks were allowed to vary in the fit, since these cannot be determined reliably by any means other than total scattering. However, the Al-Al peaks are relatively small and





The experimental differential correlation function, $D_{exp}(r)$, for Al₂O₃ (black continuous line). (a) Also shown are the total function (blue) fitted over the distance range 0.50–3.58 Å, the fitted average density term (black dashed line) and the residual (black continuous line, with values close to zero) over the range of the fit. (b) Also shown are the individual component peaks of the fit, using the same colour key for pairs of elements as in Fig. 4(b).

Structural parameters (interatomic distance, r_{jk} , coordination number, n_{jk} , and RMS variation in distance, $\langle u_{jk}^2 \rangle^{1/2}$) for the fit to the experimental differential correlation function, $D_{exp}(r)$, for Al₂O₃ over the distance range from 0.50 to 3.58 Å.

Blank lines are used to separate the distances for each peak manifold in the correlation function. The interatomic distances and coordination numbers for the average structure, according to a literature report of the crystal structure (Thompson *et al.*, 1987), are given, and only the Al-O distances were refined in the fit. The coordination numbers were not refined in the fit. (Statistical errors from the fits are given in parentheses.)

	r_{jk} (Å)				
Atom pair <i>j–k</i>	Average structure	Fit	n _{jk}	$\langle u_{jk}^2 \rangle^{1/2}$ (Å)	Structural description
$(Al-O)_1$	1.852	1.8550 (8)	3	0.061 (1)	Short bond in AlO ₆ octahedron
$(Al-O)_2$	1.973	1.9691 (9)	3	0.076 (1)	Long bond in AlO_6 octahedron
$(O-O)_1$	2.540		2	0.076 (2)	Edges of face shared between two octahedra
$(0-0)_{2}$	2.623		2	0.094 (2)	Edge shared between two octahedra
$(Al - Al)_1$	2.645		1	0.12 (3)†	Distance across shared face
$(O - O)_3$	2.722		4	0.086 (4)	Octahedron edge, not shared with another octahedron
$(Al - Al)_2$	2.789		3	0.12 (3)†	Distance across shared edge
$(O-O)_4$	2.857		4	0.077 (3)	Octahedron edge, not shared with another octahedron
(Al-O) ₃	3.227	3.218 (1)	3	0.07(1)	Second Al–O shell (<i>i.e.</i> Al–O–Al–O)
(Al-Al) ₃	3.223		3	0.08 (5)‡	Distance across shared corner
$(Al-O)_4$	3.430	3.43 (2)	3	0.068 (6)	Second Al–O shell (<i>i.e.</i> Al–O–Al–O)
$(Al - Al)_4$	3.498		6	0.08 (5)‡	Distance across shared corner
$(Al-O)_5$	3.548	3.56 (2)	3	0.063 (3)	Second Al–O shell (<i>i.e.</i> Al–O–Al–O)

† Values constrained to be equal. ‡ Values constrained to be equal.

Table 6

Results (normalization factor, $f_{\rm norm}$, and Al scattering length, $\overline{b}_{\rm Al}$) from fitting the experimental differential correlation function, $D_{\rm exp}(r)$, for Al₂O₃ over the distance range from 0.50 to $r_{\rm max}$ (statistical errors from the fits are given in parentheses).

r _{max} (Å)	$f_{\rm norm}$	\overline{b}_{Al} (fm)
1.60	1.0†	3.10 (4)
2.25	1.052 (9)	3.35 (3)
2.89	1.082 (5)	3.44 (2)
3.58	1.082 (4)	3.44 (1)

† Fixed.

hence it was found to be necessary to constrain the values of $\langle u_{A1A1}^2 \rangle^{1/2}$ in each region to be equal, for a reasonable result to be obtained. The atom number density, $g^0 = 0.1177$ atoms Å⁻³, determined from the crystal structure (Thompson *et al.*, 1987) was used in the calculation of the fitted function [equation (3)].

 $D_{exp}(r)$ for Al₂O₃ was fitted using a modified version of a standard program for fitting neutron correlation functions (Hannon, 2013c), which allowed the scattering length and normalization factor to be varied, and the structural parameters obtained are given in Table 5. For the fit, the normalization factor was $f_{\text{norm}} = 1.082$ (4), within the expected normalization range of $\pm 10\%$, and the scattering length of aluminium was $\overline{b}_{Al} = 3.44$ (1) fm (see Table 6). This value of \overline{b}_{A1} agrees closely with the literature value 3.449 (5) fm (Rauch & Waschkowski, 2002), showing that the method is capable of determining a scattering length value well. The fitting program evaluates statistical errors on the fitted parameters and these are given in the tables. The experimental errors on the known scattering lengths have not been allowed for in our fitting or in the estimation of the errors on the fitted \overline{b} values. However, it is of note that the experimental error on the value of b for oxygen is relatively small (see Table 1) and

consequently its influence is small, showing why oxides are a good choice of material for this method.

The first peak of $D_{exp}(r)$ for Al₂O₃ has a small but significant asymmetry and its shape could not be adequately described by using a single distance to represent the average Al–O bond length. This is because the difference in the two bond lengths, 0.1141 Å, is significant in comparison with the FWHM for the real-space resolution of the measurement. On the other hand, the fitted Al–O bond lengths differ very little from those for the average structure (see Table 5), in contrast to the situation for phases of SiO₂, where correlated atomic motions cause a significant difference (Dove *et al.*, 1997); the effect is much larger in SiO₂ because it has a smaller coordination number and stronger bonds, and a structure that more readily accommodates coupled rotations of the structural units (Buchenau *et al.*, 1984).

In order to investigate what distance range needs to be fitted to yield a satisfactory value for the scattering length, several fits were performed over the distance range from 0.50 Å to $r_{\rm max}$, for several different values $r_{\rm max}$, yielding the parameters f_{norm} and \overline{b}_{Al} given in Table 6. Each value of r_{max} was chosen to include a different number of peak manifolds. The detailed structural parameters for these fits are given in Tables S1 and S2, and are almost identical to those given in Table 5, whilst the fits are shown in Figs. S2, S3 and S4. Note that the fit with $r_{\text{max}} = 1.60$ Å is the same as a fit for a monatomic system, in that f_{norm} cannot be varied in the fit, and thus it shows the kind of result that might be obtained for a monatomic sample with data that can be corrected well. As the value of r_{max} is increased, the value for the scattering length \overline{b}_{A1} improves, in terms of both its experimental error and its closeness to the literature value. We conclude that the fit should include the low-r region, the nearest-neighbour peak and at least the first complex peak manifold, in order to realize

its full potential for scattering length determination. Clearly, it is beneficial for the fitting to include regions with different dependences on the scattering length of interest.

4.4. Determination of \overline{b} for isotopes of Ir

The compound Sr_2IrO_4 is well suited to the determination of \overline{b} for Ir because it has a relatively simple crystal structure, with two O sites, and one site each for Sr and Ir (see Table 3). As for Al in Al₂O₃, the Ir atoms are octahedrally coordinated by oxygen, and for this higher coordination the local structure deviations from the average structure are likely to be small. Furthermore, there is no evidence for partial occupancy of any of the atomic sites.

The experimental corrections for the isotopically enriched sample of Sr_2IrO_4 are much more severe than for Al_2O_3 , because of the high absorption associated with ¹⁹³Ir, and the Qrange of the experimental data is much more restricted, owing to the absorption resonance of the small residue of ¹⁹¹Ir. Fig. 7 shows the experimental differential correlation function, $D_{exp}(r)$, of isotopically enriched Sr_2IrO_4 calculated using the step modification function (Hannon, 2015) with a value of



The experimental differential correlation function, $D_{exp}(r)$, for isotopically enriched Sr₂IrO₄ (black continuous line). (a) Also shown are the total function (blue) fitted over the distance range 0.70–3.40 Å, the fitted average density term (sloping black long-dashed line) and the residual (black continuous line, displaced vertically by -1.6 units for visibility, with the zero level shown as a horizontal black short-dashed line) over the range of the fit. (b) Also shown are the individual component peaks of the fit, using the same colour key for pairs of elements as in Fig. 5(b).

23 Å⁻¹ for Q_{max} . The relatively small value of Q_{max} was required as a result of the absorbing effect of the ¹⁹¹Ir resonance, which obscures the higher-Q region. The smaller value of Q_{max} (compared with the results for Al₂O₃) leads to a broader resolution in real space, which was improved to some extent by the use of the step modification function [rather than the Lorch function (Lorch, 1969)], at the expense of significant termination ripples. Although the termination ripples cause $D_{\text{exp}}(r)$ to be less visually appealing (particularly at low r), they are included in the fitting procedure and therefore they are not a significant difficulty for the fit. For this modification function and value of Q_{max} , the real-space resolution has an FWHM of 0.165 Å.

The experimental differential correlation function, $D_{exp}(r)$, of isotopically enriched Sr₂IrO₄ was fitted with a minimum distance of 0.70 Å, using a similar procedure to that used for Al₂O₃. The parameters for a fit with a maximum distance of 3.40 Å are given in Table 7, and the fit itself is shown in Fig. 7. According to the Rietveld structure determination given in Table 3, there is a small difference between the equatorial (1.979 Å) and axial (2.060 Å) Ir-O bond lengths. However, this difference (0.081 Å) is small compared with the real-space resolution and asymmetry of the Ir-O peak is not apparent in $D_{exp}(r)$. Therefore a single Ir-O peak at a suitably averaged distance was used for the fit. Since the two Ir-O bond lengths are similar, it is reasonable to assume that their thermal widths, $\langle u_{\rm IrO}^2 \rangle^{1/2}$, are similar too. Only the peak widths, $f_{\rm norm}$ and \overline{b}_{iso} were varied in the fit, whilst all the interatomic distances were held fixed. Also the widths of the O-O peaks were constrained to be equal. The atom number density, $g^0 =$ 0.07188 atoms $Å^{-3}$, determined from the Rietveld structure determination (Table 3), was used in the calculation of the fitted function [equation (3)].

For the fit shown in Fig. 7 and Table 7, the normalization factor was $f_{\rm norm} = 0.89$ (1); although this value is slightly outside the expected range of $\pm 10\%$, it is likely that this is due to the relatively severe effects of absorption. The fit yields a scattering length for ^{iso}Ir of $\overline{b}_{\rm iso} = 9.77$ (17) fm. The error on this value is larger than that for $\overline{b}_{\rm Al}$, and it is likely that this is a consequence of the high absorption for this sample. Nevertheless, it is worth noting that this error is smaller than that of the literature value for the scattering length of ^{Nat}Ir (see Table 1).

Similarly to the fitting for Al_2O_3 , several fits were performed over the distance range from 0.70 Å to r_{max} , with values of r_{max} chosen to include different numbers of peak manifolds, yielding the parameters f_{norm} and \overline{b}_{iso} given in Table 8. The detailed structural parameters for the fits are given in Tables S3, S4 and 7, whilst the fits are shown in Figs. S5, S6, S7 and 7. As for Al_2O_3 , a larger value of r_{max} leads to a smaller experimental error for \overline{b}_{iso} , and we conclude that our best result [$\overline{b}_{iso} = 9.77$ (17) fm] was obtained with $r_{max} =$ 3.40 Å (see Table 7 and Fig. 7).

Fig. 2(b) shows a Rietveld refinement that was performed identically to the refinement discussed in §4.1, with the sole exception that the Ir scattering length was fixed at the value of 9.77 fm obtained from the correlation function fit, and the

Structural parameters (interatomic distance, r_{jk} , coordination number, n_{jk} , and RMS variation in distance, $\langle u_{jk}^2 \rangle^{1/2}$) for the fit to the experimental differential correlation function, $D_{exp}(r)$, for isotopically enriched Sr₂IrO₄ over the distance range 0.70–3.40 Å.

Blank lines are used to separate the distances for each peak manifold in the correlation function. The interatomic distances and coordination numbers, obtained by Rietveld refinement (Table 3), are given and were not refined in the fit. (Statistical errors from the fits are given in parentheses.)

Atom pair <i>j–k</i>	r_{jk} (Å)	n_{jk}	$\langle u_{jk}^2 \rangle^{1/2}$ (Å)	Structural description
Ir–O	2.005†	6	0.069 (2)	Average Ir–O distance in IrO ₆ octahedron
$(Sr-O)_1$	2.475‡	3	0.087 (3)	Shortest bond in irregular SrO ₉ polyhedron
$(Sr-O)_2$	2.752	4	0.116 (5)	Intermediate bond in irregular SrO ₉ polyhedron
$(O-O)_{1}$	2.798	2	0.099 (3)§	O2-O2 distance between any pair of equatorial O atoms in IrO ₆ octahedron
$(0-0)_{2}$	2.857	4	0.099 (3)§	O1-O2 distance from axial oxygen to equatorial oxygen in IrO ₆ octahedron
$(Sr-O)_3$	3.009	2	0.118 (10)	Longest bond in irregular SrO ₉ polyhedron
$(O-O)_{3}$	3.139	0.5	0.099 (3)§	O2–O2 distance in SrO ₉ polyhedron
Ir—Sr	3.352	8	0.089 (2)	Ir-Sr distance across shared face between IrO6 octahedron and SrO9 polyhedron

 \dagger Value is an appropriately weighted average for equatorial and axial Ir-O bonds. \ddagger Value is an appropriate average of two closely similar Sr-O bond lengths. \$ Values constrained to be equal.

Table 8

Results (normalization factor, $f_{\rm norm}$, and scattering length of isotopically enriched Ir, $\bar{b}_{\rm iso}$) from fitting the experimental differential correlation function, $D_{\rm exp}(r)$, for isotopically enriched Sr₂IrO₄ over the distance range from 0.70 Å to $r_{\rm max}$ (statistical errors from the fits are given in parentheses).

$\overline{b}_{\rm iso}~({\rm fm})$
9.03 (66)
10.76 (44)
9.75 (18)
9.77 (17)
_

† Fixed.

Rietveld fit appears indistinguishable from the earlier Rietveld fit (Fig. 2a). This value of \overline{b}_{iso} from the correlation function fit is well within the central plateau of R_{wp} shown in Fig. 3, and is thus consistent with Rietveld refinement when the correlation between parameters is taken into account. The scattering length value determined from fitting the correlation function depends essentially on the relative areas under the peaks, not the peak heights or widths. Therefore, errors in the fitted widths of the correlation function peaks (*i.e.* the $\langle u_{ik}^2 \rangle^{1/2}$ values in Tables 5 and 7) should not have a significant effect on the value of the fitted scattering length. Thus, the scattering length determined from fitting the correlation function does not suffer from the unreliability that affects the result from Rietveld refinement (due to correlation between parameters see §4.1) and hence the correlation function value is to be preferred. This difference between the two analysis methods essentially arises as a consequence of the Fourier transformation given in equation (2): Rietveld refinement is used to fit data in reciprocal space, where the Debye–Waller factor acts to reduce the intensities of peaks. On the other hand, the correlation function is a real-space function, the peaks of which are convoluted by the (thermal) disorder, and hence their intensities are not reduced [see equation (5)].

It is advantageous that Ir has only two naturally occurring, stable isotopes, so that the scattering lengths of natural Ir and our isotopically enriched metal are given in terms of the scattering lengths of the two isotopes by

$$\overline{b}_{\text{Nat}} = f_{\text{Nat}} \overline{b}_{193} + (1 - f_{\text{Nat}}) \overline{b}_{191} \text{ and}$$
$$\overline{b}_{\text{iso}} = f_{\text{iso}} \overline{b}_{193} + (1 - f_{\text{iso}}) \overline{b}_{191}, \tag{8}$$

where f_{Nat} and f_{iso} are, respectively, the abundance of ¹⁹³Ir in ^{Nat}Ir and in the enriched metal, ^{iso}Ir. These two abundances are known (see Table 1 and §2), and hence the two simultaneous equations of (8) can be solved to yield the scattering lengths of the two isotopes: $\overline{b}_{193} = 9.71$ (18) fm and $\overline{b}_{191} = 12.1$ (9) fm. The error on \overline{b}_{191} is much larger than the error on \overline{b}_{193} , firstly because \overline{b}_{iso} has a smaller error than \overline{b}_{Nat} , and secondly because ¹⁹¹Ir is a minority constituent of both ^{iso}Ir and ^{Nat}Ir.

In general, the incoherent cross section of an element has contributions due to both spin incoherence and isotope incoherence (Squires, 1978). For a single isotope, i, with nuclear spin I_i , the average values of the scattering length and squared scattering length for nuclei of this isotope are given by

$$\overline{b}_{i} = \frac{(I_{i}+1)b_{i}^{+} + I_{i}b_{i}^{-}}{2I_{i}+1} \quad \text{and} \quad \overline{b}_{i}^{2} = \frac{(I_{i}+1)(b_{i}^{+})^{2} + I_{i}(b_{i}^{-})^{2}}{2I_{i}+1},$$
(9)

where b_i^+ and b_i^- are the scattering lengths of the two possible states (with spin $I_i + \frac{1}{2}$ or $I_i - \frac{1}{2}$, respectively) of the compound nucleus-neutron system. The element then has a scattering length and total scattering cross section given by

$$\overline{b} = \sum_{i} f_i \overline{b}_i$$
 and $\sigma_{\text{scatt}} = 4\pi \sum_{i} f_i \overline{b}_i^2$, (10)

where f_i is the abundance of isotope *i*. The incoherent cross section of the element is given by

$$\sigma_{\rm incoh} = \sigma_{\rm scatt} - \sigma_{\rm coh} = \sigma_{\rm scatt} - 4\pi \overline{b}^2.$$
(11)

The incoherent cross section, σ_{incoh} , for natural Ir is tabulated as 0.0 with an experimental error usually given as 3.0 (see Table 1), although the original published report (Mueller *et al.*, 1963) gives no indication of the experimental error. Consideration of equations (9), (10) and (11) shows that if σ_{incoh} for the element is exactly zero then this can only occur if b_i^+ and b_i^- have the same value for all the isotopes of the element. Thus, the fact that experiment (Mueller *et al.*, 1963) shows that the value of σ_{incoh} is small implies that the scattering lengths of the two isotopes must be similar to the scattering length of the natural element; our values of 9.71 (18) and 12.1 (9) fm for the scattering lengths of ¹⁹³Ir and ¹⁹¹Ir are similar to the value of 10.6 (3) fm for ^{Nat}Ir, and therefore our values are shown to be reasonable. The actual value of σ_{incoh} for ^{Nat}Ir cannot be deduced from these three scattering length values, but the smallest possible value that is consistent with them is 0.17 barn, and this is reasonable in comparison with the tabulated value of 0.0 (3.0) barn (see Table 1).

Our analysis has shown that it is advantageous to fit D(r) up to a larger maximum distance, r_{max} . However, one factor that we have not taken into account is the effect of experimental Qresolution, which leads to the features in D(r) being increasingly damped as r increases (Grimley *et al.*, 1990; Toby & Egami, 1992; Tucker *et al.*, 2001), and it may be necessary to consider this effect if the method is extended to longer distances. Nevertheless, the Q resolution of the GEM diffractometer is high (Hannon, 2005), and thus for the relatively small range in r used for the analysis reported here the effect of Q resolution will be small.

A possible advantage of the scattering length measurement method introduced here is that it is based on diffraction, the same experimental technique as that for which the value of \overline{b}_{iso} is likely to be used. Although conventional crystallographic methods have been used before to determine scattering lengths, this is the first reported use of total scattering methods to determine a scattering length.

We have been able to deduce values for the scattering lengths of both isotopes of Ir, and hence our results make it possible to obtain a value of the Ir scattering length for a sample enriched in ¹⁹³Ir with any specified value of the enrichment factor, f_{iso} [see equation (8)]. Thus, our results make it possible for the first time to take full advantage of the potential benefit (reduced absorption) for ND that arises from enrichment in ¹⁹³Ir, and this may lead to advances in the study of iridates by ND.

5. Conclusions

It has been proposed that a relative value for the bound coherent neutron scattering length, \overline{b} , of an element can be determined from a total scattering neutron diffraction measurement on a suitable oxide crystal powder of known structure. This is achieved by suitable fitting of the neutron correlation function, for which it is essential to take into account the contribution from the average density of the sample. The capability of the method has been demonstrated and verified using a measurement on the corundum form of Al₂O₃ to obtain a value $\overline{b} = 3.44$ (1) fm for Al, in good agreement with the literature value of 3.449 (5) fm. It has been shown that, to realize the full potential of the method, the fit should cover a range of interatomic distances that starts from a minimum value significantly below the shortest distance in the sample, and has a maximum value sufficiently large to include both the nearest-neighbour contribution and the first

complex manifold of peaks in the correlation function. The method has been applied to the isotopes of Ir, for which the values of the scattering lengths were unknown and which are difficult to investigate because of the large absorption cross sections. Values of $\overline{b} = 9.71$ (18) fm and $\overline{b} = 12.1$ (9) fm for ¹⁹³Ir and ¹⁹¹Ir, respectively, have been determined from the neutron correlation function of a sample of Sr_2IrO_4 enriched in ¹⁹³Ir. The Ir scattering length has also been determined by Rietveld refinement of the neutron diffraction pattern of isotopically enriched Sr₂IrO₄, yielding a similar result to that obtained from fitting the correlation function. The result from Rietveld analysis, however, is shown to suffer from uncertainty due to correlation between parameters in the fit. The values obtained for the scattering lengths of the two Ir isotopes are shown to be consistent with the tabulated scattering length and cross sections of natural Ir, and imply a small incoherent cross section for natural Ir. The measurement of the scattering lengths of these two isotopes permits the use of samples enriched in ¹⁹³Ir to obtain significantly better neutron diffraction results on iridates than was hitherto possible.

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