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Neutron Compton scattering from the super proton conductor $\text{H}_3\text{OSbTeO}_6$ and polyethylene: a comparison of proton momentum distributions and reduced cross-sections

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Abstract

Neutron Compton scattering (NCS) results at large momentum transfers ($q \approx 60\text{--}130 \text{ \AA}^{-1}$) obtained from the super proton conductor $\text{H}_3\text{OSbTeO}_6$ (powder at $T = 295 \text{ K}$) are compared with those obtained from polyethylene (PE, foil at $T = 295 \text{ K}$). The Compton profiles of protons in both systems are approximately Gaussians with equal widths, $\sigma_{\text{H}} \approx 5 \text{ \AA}^{-1}$, within experimental error, thus indicating that the effective (averaged over all spatial directions) Born–Oppenheimer (BO) potentials of protons in both systems are similar. In contrast, the anomalous decrease of scattering intensity from H in $\text{H}_3\text{OSbTeO}_6$ is only about 50% of that observed in PE. In a proposed theoretical frame (based on the violation of the BO approximation and attosecond proton–electron quantum entanglement) these comparative results reveal that the more mobile protons of the proton conductor are subject to a significantly faster decoherent quantum dynamics, which naturally causes a reduction of the anomaly in the scattering intensity. These new results may contribute to testing the validity of competing theoretical models. Connection with related NCS results from the super proton conductor $\text{Rb}_3\text{H}(\text{SO}_4)_2$ is briefly made.

1. Introduction

Several neutron Compton scattering (NCS, also known as deep inelastic neutron scattering, DINS) experiments on liquid and solid samples containing protons or deuterons show a striking anomaly, which is a shortfall in the intensity of epithermal neutrons scattered by the protons and deuterons; cf [1–7]. For example, neutrons colliding with water for just 100–500 as will

see a ratio of hydrogen to oxygen of roughly 1.5 to 1, instead of 2 to 1, corresponding to the chemical formula H_2O [1]. Due to the large energy and momentum transfers applied, the duration of a neutron–proton scattering event is a fraction of a femtosecond which is extremely short compared to condensed-matter relaxation times. The experiments were performed at the ISIS neutron spallation facility, UK.

Recently this surprising effect has been confirmed [6, 7] using an independent method, electron–proton Compton scattering (ECS), at the Australian National University. ECS experiments from a solid polymer showed the exact same shortfall in scattered electrons (with initial energy about 20–35 keV) from hydrogen nuclei, comparable to the shortfall of scattered neutrons in accompanying NCS experiments on the same polymer. The similarity of the results is striking because the two projectiles interact with protons via fundamentally different forces—electromagnetic and strong [8].

Certain theoretical considerations [9–11] suggest the presence of attosecond quantum entanglement of the scattering protons and the surrounding electrons, and that the usual adiabatic Born–Oppenheimer (BO) approximation is not applicable [3, 13–15]. It was proposed [9] that the relevant theoretical frame for the description of the considered effect may be given by the dynamics of open quantum systems, which exhibit non-unitary time evolution [12]; see also section 4.

Due to its novelty and far-reaching consequences, however, this new scattering effect has been the focus of various criticisms, cf [18, 19]. Therefore, considerable work to identify possible sources of experimental and data-analysis errors was made, which succeeded in demonstrating the excellent working conditions of the spectrometer Vesuvio at ISIS [20, 21]. Moreover, a novel approach was recently invented by Dorner [22, 23] to check independently the validity of the striking experimental results. The Dorner method is a model-free data-reduction scheme that is independent of the form of momentum distribution of target nuclei and instrument resolution function [22–24]. It was demonstrated, through numerical analysis of NCS data collected on polyethylene [4] and metallic hydrides [2], that both (a) the usual convolution approximation (CA) being applied in the frame of the standard data-reduction scheme of ISIS [20] and (b) the new Dorner method yield the same scattering intensities, thus providing strong support for the effect under consideration [22, 24].

Extending our earlier NCS investigations, we recently started research on super proton conductors, a class of materials which are also of interest for the technology of fuel cells. Here we present, for the first time, a comparison of results which are based on NCS measurements on the super proton conductor $\text{H}_3\text{OSbTeO}_6$ (see below) and the organic polymer polyethylene, $(-\text{CH}_2-)_n$. A particularly interesting finding revealed by the present experiments may be summarized as follows: within experimental error, we found (1) equal proton Compton profiles in these materials and (2) at the same time, very different anomalous scattering intensities off protons, which differ by a factor of two. This comparison may have considerable consequences for various theoretical models [9–17] of the anomalous scattering effect [1–7] under consideration; see also section 4.

2. Experimental details

2.1. The super proton conductor $\text{H}_3\text{OSbTeO}_6$

$\text{H}_3\text{OSbTeO}_6$ is a fast proton conductor at ambient temperature [25] with a very good specific proton conductivity of 0.1 S cm^{-1} . It was prepared by ion exchange from KSbTeO_6 (synthesized by solid state reaction of $\text{K}_2\text{C}_2\text{O}_4$, Sb_2O_3 , and TeO_2) using concentrated sulfuric acid (453 K, 12 h) [25]. The product was then washed with distilled water. After two cycles,

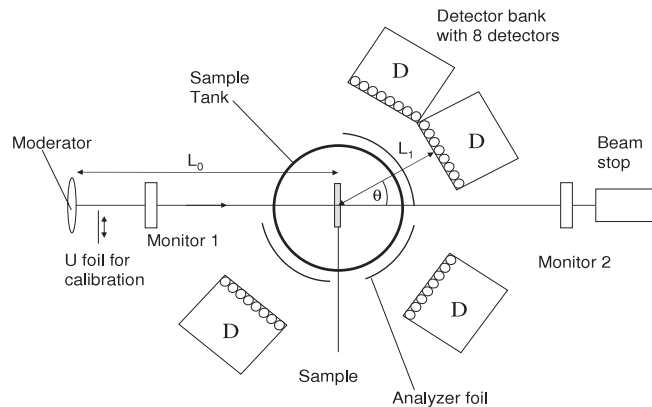


Figure 1. A schematic representation of the Vesuvio spectrometer at ISIS.

no potassium could be detected by x-ray fluorescence analysis (XRF). Chemical analysis (combustion method) resulted in a hydrogen amount of 0.83(1)wt% which is exactly the theoretical value calculated from the chemical formula. The x-ray powder diffraction (XRD) pattern showed single phase $\text{H}_3\text{OSbTeO}_6$, crystallizing in a cubic defect pyrochlore type structure, and all protons are symmetrically equivalent and equally mobile [25].

2.2. The Vesuvio spectrometer

The NCS measurements have been carried out at the Vesuvio inverse geometry time-of-flight (TOF) spectrometer [26, 27], at the ISIS spallation neutron source. On this instrument a ‘white’ neutron beam with a $1/E^{0.9}$ energy dependence in the epithermal region, is directed towards the sample position, located at a distance $L_0 \approx 11$ m from the 295 K water moderator. The sample–detector distances L_1 were about 70 cm. The spectrometer is equipped with four banks of ^6Li glass scintillators placed in an angular range of about 35° – 70° . The energy of the scattered neutrons was selected by means of filter analysers, in the form of ^{197}Au foils, that resonantly captured neutrons over narrow energy intervals (resonances). The experimental scattering signal is then reconstructed using the single difference technique [28], which accomplishes neutron measurements with and without the filter analysers placed between the sample and the detectors; see figure 1 for a schematic drawing. The experimental signal acquired is a TOF spectrum and a well established standard data-reduction scheme is applied to the data [20].

3. Results

The analysis of the measured TOF spectra was carried out using the standard data-reduction routines available at ISIS (also taking into account final state effects (FSE) [29, 20]), as well as data-analysis routines developed in our laboratory. The samples (flat slabs) were about 0.1–0.2 mm thick and put perpendicular to the incoming beam. (Earlier experiments on polyethylene with samples perpendicular to the beam and other ones tilted by about 20° gave identical results; see [4].) The scattering power was kept at about 10% or less. The results presented below were obtained from 16 detectors at ‘large’ scattering angles, $\theta = 50^\circ$ – 70° , and correspondingly at large momentum transfers, $q = 58$ – 134 \AA^{-1} . As a consequence, the separation of the H peak from that of the heavier atoms is very good. Due to the large momentum transfers applied, the impulse approximation (IA) is known to be valid [20, 29–31].

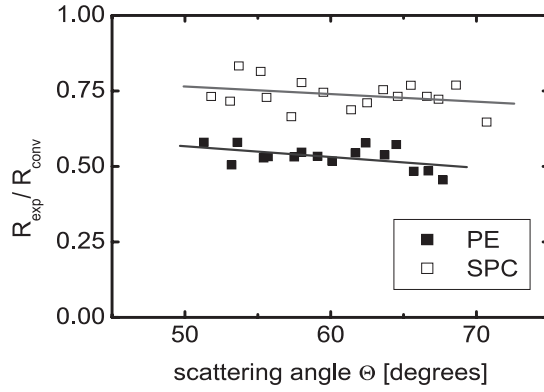


Figure 2. Anomalous scattering intensity from protons. PE: polyethylene; SPC: the super proton conductor $\text{H}_3\text{OSbTeO}_6$. $R_{\text{exp}} = A_H/A_X$: ratio of measured areas A_H of the H peak and heavy-atom(s) peak A_X . R_{conv} : expected value of this ratio according to conventional theory. The squares represent experimental data. The straight lines are linear least-square-fits to the data. The anomalous scattering intensity effect is considerably larger (about two times) in PE than in SPC.

The analysis of the TOF spectra yields the ratio of intensities

$$R_{\text{exp}} = \frac{A_H}{A_X} \quad (1)$$

that is, the ratio of integrated intensities of the H peak (A_H) with that of the heavy-atom(s) peak (A_X). For the SPC, the latter is due to scattering from O, Sb and Te, because the corresponding peaks are not resolved in the TOF spectra. For the PE sample, the heavy-atom peak is due to scattering off carbon. The theoretically expected value of A_j (for $j = H, X$) is proportional to the particle density N_j of atoms j times the ‘bound’ total cross-section $4\pi b_j^2$ for these atoms [20]. Thus the theoretically expected value R_{conv} of the considered ratio is given by

$$R_{\text{conv}} = \frac{N_H b_H^2}{N_X b_X^2} \quad (2)$$

(b_j is the ‘bound’ scattering length.) For the SPC, using tabulated values [32] for the cross-sections (in barn, b) one obtains $R_{\text{conv}}(\text{SPC}) = 3 \times 82.02b / (7 \times 4.232b + 3.90b + 4.32b) = 6.502$ and accordingly for PE, $R_{\text{conv}}(\text{PE}) = 2 \times 82.02b / 6.646b = 24.68$. For a detailed derivation of these formulae, see e.g. [20].

Figure 2 shows the anomalous scattering intensity effect [1–7] of protons of the super proton conductor (SPC) $\text{H}_3\text{OSbTeO}_6$ (polycrystalline) and of polyethylene (PE), at room temperature. Both materials exhibit strong deviations from conventional theoretical expectation, since $R_{\text{exp}} \neq R_{\text{conv}}$. Remarkably, the ‘anomalous’ decrease of scattering intensity from H found in PE is some two times larger than the corresponding one found in the SPC. The shown lines through the data points are linear least-square fits. In both materials there seems to exist the same slight angular dependence of the considered effect on scattering angle θ , and thus on momentum transfer $\hbar q$, although it appears to be within the experimental errors of these two experiments. However, almost the same slight angular dependence of R_{exp} was recently observed in two other solid materials at room temperature, i.e. $(\text{NH}_4)_2\text{PdCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ [33]. To further investigate this issue, more precise data (i.e. much longer beam times) would be needed.

The comparison of these results appears to be particularly interesting in the light of the data shown in figure 3. Here are presented the widths σ_H of the proton Compton profiles (termed $J(y)$ in the literature; see e.g. [20, 29]) by fitting the corresponding data with Gaussians; this

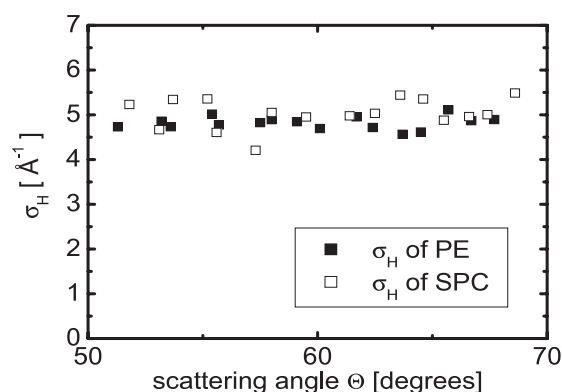


Figure 3. Widths of Compton profiles. PE: polyethylene; SPC: the super proton conductor $\text{H}_3\text{OSbTeO}_6$. Comparison of NCS results in the scattering angle range 50° – 70° , corresponding to $q = 58$ – 134\AA^{-1} , with very good peak separation. σ_H : standard deviation (width) of the measured H Compton profiles fitted with Gaussians. Note that the measured widths for both materials are equal, within experimental error. The constancy of σ_H over scattering angle θ shows the validity of y -scaling (and impulse approximation); see [20, 31, 29].

procedure is completely sufficient within present experimental error. The measured widths of the Compton profiles for both materials were found to be equal, within experimental error. The constancy of $\sigma_H \approx 5 \text{\AA}^{-1}$ over scattering angle θ should be stressed; see below. Note that the data analysis takes final state effects (FSE) [29] into account.

4. Discussion

The constancy of σ_H over scattering angle (and thus over momentum transfer) for both materials, as shown in figure 3, should be noted. This demonstrates that y -scaling [20, 29] applies very well to these data sets. This finding is in line with the validity of the impulse approximation (IA) [20, 31, 29, 30], the latter being widely used in NCS investigations. As is well known, FSE play only a minor role at the high momentum transfers of our experiments. According to the insightful theoretical analysis of NCS by Mayers [30], this constancy can be taken as evidence that also initial state effects (ISE) are negligible here.

Moreover, both materials appear to have the same value of σ_H ; see figure 3. This implies that both effective BO potentials (averaged over all spatial directions, since the samples are not monocrystalline) of a proton of PE and SPC in its ground state should be very similar; cf [31].

In contrast to this finding, the anomalously reduced scattering cross-section density of H in the fast proton conductor SPC is considerably less pronounced than in PE; see figure 2. This comparison is of particular interest, since it indicates that the ‘static’ local environment of a proton (as represented by its effective BO potential) should not be the only reason for the anomalies in the scattering intensity. This observation is in line with the ‘quantum dynamical’ picture proposed in [3, 9, 10], according to which the H^+ transport phenomenon in the proton conductor may be accompanied and/or governed by a new proposed mechanism, i.e. attosecond entanglement of protons with adjacent electrons and associated decoherence due to the environmental interactions. The preceding comparison of results is consistent with the expectation that the more mobile protons of SPC may experience variations of their local environment; thus they are much more subject to decoherence (and/or dephasing) [12] than the immobile protons in the covalent C–H bonds of PE (which is not a proton conductor).

In this connection, another proposed interpretation [13–15] of the considered anomalous NCS intensity effect should be mentioned. This is based on the assumption that, due to the high energy transfers of NCS, the neutron–proton collision may result in non-adiabatic electronic excitation which would shift part of the neutron intensity to higher transfer energies $\hbar\omega$ [13, 14]. This physical picture is tantamount to the violation of the well known BO approximation; see also [3]. In the frame of the models of [13, 14], the strong difference between the reduced scattering cross-section densities of H found in SPC and PE, as shown in figure 2, implies that the violation of the BO approximation in these two materials should have strongly differing characteristics. The elucidation of the latter should provide considerably more physical insight into the theoretical models under consideration.

Additionally, further theoretical work by Gidopoulos [15] shows various interesting features, e.g. a ‘deformation’ of the high-energy tail of the Compton profile and dynamic structure factor $S(q, \omega)$ caused by the aforementioned shifted intensity. Moreover, a related deformation of the H peak seems consistent with the quantum dynamical model of [9, 10], in which attosecond quantum entanglement and decoherence play a major role. This is because the scattering time τ_{scatt} of the neutron–proton collision (being q -dependent [31]) varies considerably over the TOF-peak shape and thus the degree of decoherence should vary too—a shorter τ_{scatt} corresponds to ‘less decoherence’ [9, 10]. The latter may then cause different intensity-reductions of the two H peak wings, thus leading to an H peak deformation as mentioned above. Obviously, these considerations imply that (i) the shape of momentum distribution (or Compton profile) and (ii) the effect of reduced cross-section of H may not be a completely independent phenomena, as often believed (see e.g. [34]).

Very recently, NCS results from the super proton conductor $\text{Rb}_3\text{H}(\text{SO}_4)_2$ (single crystal) were published [35]. From the presented data one finds the averaged (over all spatial directions) width of the H Compton profile to be $\sigma_{H,\text{ave}} \approx 4.24 \text{ \AA}^{-1}$ and 4.26 \AA^{-1} , for $T = 10 \text{ K}$ and 70 K , respectively. These widths are considerably smaller than that in our case, i.e. $\sigma_H \approx 5 \text{ \AA}^{-1}$ (measured at room temperature). In the conventional theoretical frame of NCS, in which the concept of effective BO potential plays a central role, these results obviously imply that the wavefunction of a proton of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ is *more delocalized* in space than that of a proton of $\text{H}_3\text{OSbTeO}_6$. At the same time, the proton-conductances of these materials exhibit quite the ‘opposite’ behaviour from the conventionally expected one. At room temperature, $\text{H}_3\text{OSbTeO}_6$ has a very high proton conductivity (0.1 S cm^{-1}), whereas $\text{Rb}_3\text{H}(\text{SO}_4)_2$ shows only a poor conductivity. (The latter becomes a super proton conductor only above 449 K , and shows a proton conductance of about 0.01 S cm^{-1} , which is one order of magnitude less than that of $\text{H}_3\text{OSbTeO}_6$; for further details, see e.g. [36–38].) Thus, one arrives at the somewhat counterintuitive conclusion that the material having more spatially localized protons is a significantly better proton conductor! Obviously, the form of the aforementioned BO potential—i.e. the one being inferred from the NCS measurement by applying conventional theory—cannot be the only one essential piece of information for the simulation of the transport of protons in the conductor.

Further, and more accurate, NCS investigations on $\text{H}_3\text{OSbTeO}_6$ and PE (and further super proton conductors) are planned, in order to investigate in detail the effects shown in figures 2 and 3, and also to extend these experimental studies into lower momentum and energy transfers (so that the covalent O–H and C–H bonds do not break, as in the present investigations, but remain intact).

In conclusion, the experimental findings presented in this paper, and especially the comparison of (the widths of) Compton profiles and of reduced scattering cross-sections of H in different materials, may stimulate further theoretical works and, in particular, contribute

to the testing of the aforementioned competing theoretical models. We also expect them to have considerable consequences for the quantum dynamical description of the transport processes of protons and/or proton–electron attosecond phenomena, in condensed matter and molecules.

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References

- [1] Chatzidimitriou-Dreismann C A, Abdul-Redah T, Streffer R M F and Mayers J 1997 *Phys. Rev. Lett.* **79** 2839
- [2] Karlsson E B, Chatzidimitriou-Dreismann C A, Abdul-Redah T, Streffer R M F, Hörvarsson B, Öhrmalm J and Mayers J 1997 *Europhys. Lett.* **46** 617
- [3] Chatzidimitriou-Dreismann C A, Abdul-Redah T and Kolarić B 2001 *J. Am. Chem. Soc.* **123** 11945
- [4] Chatzidimitriou-Dreismann C A, Abdul-Redah T, Streffer R M F and Mayers J 2002 *J. Chem. Phys.* **116** 1511
- [5] Karlsson E B, Abdul-Redah T, Streffer R M F, Hjörvarsson B, Mayers J and Chatzidimitriou-Dreismann C A 2003 *Phys. Rev. B* **67** 184108
- [6] Chatzidimitriou-Dreismann C A, Vos M, Kleiner C and Abdul-Redah T 2003 *Phys. Rev. Lett.* **91** 057403
- [7] Vos M, Chatzidimitriou-Dreismann C A, Abdul-Redah T and Mayers J 2005 *Nucl. Instrum. Methods B* **227** 233
- [8] Schewe P, Riordon J and Stein B 2003 Physics news update *The AIP Bulletin of Physics News* **648** 1
Schewe P, Riordon J and Stein B 2005 Physics news update *The AIP Bulletin of Physics News* **732** 2
See also Schewe P, Riordon J and Stein B 2003 *Physics Today* **56** (9) 9 (section: Physics Update)
Saunders F 2005 *Am. Sci.* **93** 411
- [9] Chatzidimitriou-Dreismann C A and Stenholm S 2005 *Decoherence, Entanglement and Information Protection in Complex Quantum Systems (NATO Science Series II vol 189)* ed V M Akulin, A Sarfati, G Kurizki and S Pellegrin (Dordrecht: Springer) pp 555–62 (Also available at: arXiv.org/abs/quant-ph/0702038)
- [10] Chatzidimitriou-Dreismann C A 2005 *Laser Phys.* **15** 780
- [11] Chatzidimitriou-Dreismann C A 2006 *Acta Phys. Hung. B* **26** 203
- [12] Breuer H-P and Petruccione F 2002 *The Theory of Open Quantum Systems* (Oxford: Oxford University Press)
- [13] Gidopoulos N I 2005 *Phys. Rev. B* **71** 054106
- [14] Reiter G F and Platzman P M 2005 *Phys. Rev. B* **71** 054107
- [15] Gidopoulos N I 2007 to be published
- [16] Karlsson E B and Lovesey S W 2000 *Phys. Rev. A* **61** 062714
Karlsson E B and Lovesey S W 2002 *Phys. Scr.* **65** 112
- [17] Karlsson E B 2003 *Phys. Rev. Lett.* **90** 095301
- [18] Blostein J J, Dawidowski J and Granada J R 2001 *Physica B* **304** 357
- [19] Cowley R A 2003 *J. Phys.: Condens. Matter* **15** 4143
- [20] Mayers J and Abdul-Redah T 2004 *J. Phys.: Condens. Matter* **16** 4811
- [21] Cowley R A and Mayers J 2006 *J. Phys.: Condens. Matter* **18** 5291
- [22] Dorner B 2006 *Nucl. Instrum. Methods B* **247** 390
- [23] Dorner B 2005 *J. Neutron Res.* **13** 267
- [24] Krzystyniak M and Chatzidimitriou-Dreismann C A 2005 *Phys. Rev. B* **72** 174117
- [25] Alonso J A and Turrillas X 2005 *Dalton Trans.* **5** 865
- [26] Mayers J, Burke T M and Newport R J 1994 *J. Phys.: Condens. Matter* **6** 641
- [27] Fielding A L and Mayers J 2002 *Nucl. Instrum. Methods A* **480** 680
- [28] Brugger R M, Taylor A D, Olsen C E, Goldstone J A and Soper A K 1984 *Nucl. Instrum. Methods* **221** 393
- [29] Sears V F 1984 *Phys. Rev. B* **30** 44
- [30] Mayers J 1990 *Phys. Rev. B* **41** 41
- [31] Watson G I 1996 *J. Phys.: Condens. Matter* **8** 5955
- [32] Sears V F 1992 *Neutron News* **3** 26
- [33] Krzystyniak M, Chatzidimitriou-Dreismann C A, Lerch M, Lalowicz Z T and Szymocha A 2007 *J. Chem. Phys.* **126** 124501
- [34] Reiter G, Burnham C, Homouz D, Platzman P M, Mayers J, Abdul-Redah T, Moravsky A P, Li J C, Loong C K and Kolesnikov A I 2006 *Phys. Rev. Lett.* **97** 247801
- [35] Homouz D *et al* 2007 *Phys. Rev. Lett.* **98** 115502

- [36] Kamimura H *et al* 2004 *Phys. Status Solidi b* **241** 61
- [37] Dolinsek J *et al* 1998 *Phys. Rev. B* **58** 8445
- [38] Fillaux F *et al* 1991 *Chem. Phys.* **154** 135