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Comment on "Magnetic Compton scattering study of Laves phase $ZrFe_2$ and Sc doped $ZrFe_2$: Experiment and Green function based relativistic calculations" by Bhatt *et al.*

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Abstract

We show how to calculate isotropic Compton profiles from sets of profiles along so-called "special directions" in the Brillouin zone computed from density-functional theory calculations, with reference to a recent paper by Bhatt et al.. We present the correct formula and demonstrate the power of special directions, highlighting the importance of carefully choosing directions and using the correct weights in obtaining accurate isotropic profiles.

Keywords: `Compton scattering, special directions in the Brillouin zone, isotropic`

A recently published paper by Bhatt *et al.* [1] has applied the technique of magnetic Compton scattering to probe the spin-density of electrons in momentum space [2]. The sensitivity to the spin-magnetic moment, and the fact that its origin can be determined (because electrons in different orbitals will have different momentum distributions) make it a powerful tool for probing magnetism in materials [2]. When Compton scattering is applied to experiments performed on single crystals, it can provide detailed and often unique information about the ground state electronic wavefunction [3] and the Fermi surface [4, 5, 6].

However, it is often the case that suitable single crystals are not available, and indeed magnetic Compton scattering measurements are often made on polycrystalline materials. In order to compare the results of these experiments with the predictions of *ab initio* density-functional theory calculations, it is essential that an isotropic momentum distribution can be computed. Recently, we described how isotropic distributions (and mean values) can be calculated using so-called "special directions" (SDs) [7]. The purpose of this comment is to show how the method should be correctly applied, using as an example the recent study by Bhatt *et al.* [1].

Many studies up to now are based on the original Houston proposal (Eq. (3) in Ref. [1]) and equations published (e.g. [8]), where some directions lying on high symmetry lines are considered together with the high symmetry directions (HSDs). Meanwhile, the isotropic distribution can be estimated much more precisely by using SDs, as proposed by Bansil [9]. We have set out this in great detail in a recent paper [7] in which we looked at cubic, hexagonal, tetragonal and trigonal structures, showing that HSDs are very inconvenient. The power of using SDs is beautifully illustrated in a paper by Prasad and Bansil [10], in which several sets (28, 36, 45, 55, and 66) of special directions for cubic lattices were proposed and discussed showing their accuracy in density-of-states and Fermi-energy evaluations in disordered alloys. Fig. 3 in Ref.[10] demonstrates the power of using SDs: 28 SD's are incomparably better than 28 sampling directions uniformly distributed over the whole Brillouin zone (BZ) or the 25 directions obtained by dividing the irreducible BZ into tetrahedra. Moreover, their results clearly indicate that even the results from 13 SDs have converged to a fairly good accuracy.

For the current calculations, we choose N-SDs (with $N = 6, 10$ [11] and $N = 15$ [12]) to check the correctness of calculating an isotropic magnetic Compton profile ($J_0(p)$) for $ZrFe_2$ depending on the number of SDs. Such directions were also considered in our previous paper [7]. We also perform calculations for the 6 directions used by Bhatt *et al.* [1] and for 1- and 3-SDs to demonstrate once more the power of SDs. For all these sets of sampling directions (shown

in Fig.1) theoretical directional magnetic Compton profiles ($J(p_z)$) were calculated; altogether, 41 such directional magnetic Compton profiles were computed [13].

In the case of the six directions applied in Ref. [1] (open squares in Fig.1), we calculated the isotropic magnetic Compton profile ($J_0(p)$) using both Eq. 4 of Ref. [1] (which is incorrect, as it has the wrong weights) and the corresponding equation with the proper weights [8], which is the following :

$$J_0(p) = 0.1088\ J_{[100]} + 0.0708\ J_{[110]} + 0.0162\ J_{[111]} + 0.3527\ J_{[210]} + 0.2877\ J_{[211]} + 0.1639\ J_{[221]} \quad (1)$$

We found that raw profiles along 10-SDs gave almost identical $J_0(p)$ as using 15-SDs. In fact, even 6-SDs approximate $J_0(p)$ very well, as can be seen in Fig. 2(b). It may seem surprising that $J_0(p)$ approximated by profiles $J(p_z)$ along only 3-SDs (triangles in Fig. 2(b)) is better than by six profiles (applying Eq.(1), denoted by full circles in Fig. 2(a)). Is this a special case related to densities in the investigated material? To answer this question we draw d coefficients (Fig. 2(c)), which define the deviation of the approximated $J_0(p)$ from its true value (for more details, see Ref. [7]). As seen, such an effect is not unexpected. Details of these 3-SDs [11] and the associated weights for calculating the isotropic $J_0(p)$ are given in Table 1, where we have (for convenience) also provided the Miller indices of directions which are very close to the special directions together with their corresponding weights.

In Fig. 3, we show $J_0(p)$ described by profiles along 15-SDs and its approximation by HSD (triangles) and only one SD (squares). As we emphasised in Ref. [7], the impact of experimental resolution needs to be carefully considered. While the resolution (full-width-half-maximum) of a typical charge Compton experiment is $\sim$ 0.1 a.u. [14], magnetic Compton typically has a resolution $\sim$ 0.4 a.u.[1, 2]. The inset to Fig. 3 shows the impact of convolution with the experimental resolution reported by Bhatt *et al.* [1]. It shows that even a single direction, but one chosen very carefully, can be better than three HSDs

[15]. HSDs are highly unprofitable and the traditional manner of calculating the isotropic average (also for such 6- or 9-sampling directions as proposed by Betts [3]) yields incomparably worse results than the use of SDs. Unfortunately, to the best of our knowledge, SDs were utilized in theoretical calculations in only a few papers.

Although we are presenting results for a small number of SDs, this does not mean that we are proposing that so few should be used to extract isotropic components from theoretical calculations. Modern computing power is such that there is little difficulty in performing calculations for e.g. 15-SDs (or even 21-SDs, if it is necessary). The coordinates and corresponding weights for these sets of SDs are given in Table 5 in [12]. However, in the case of experimental investigations the situation is quite different and here we should address the following question: In a fixed measuring time, is it more reasonable to measure a higher number of profiles with a lower statistical precision, or fewer profiles with a higher statistical precision?

The answer depends what we want to get because by measuring single crystals we could reproduce as faithfully as possible both the isotropic component $J_0(p)$ and the anisotropy of the system. It is clear that the isotropic $J_0(p)$ should be better determined by a greater number of projections and to get that the best solution is to measure a polycrystalline sample. However, in the case of anisotropic components the situation could be quite the opposite. Adding a projection at the cost of poorer statistical precision of other projections can lead to worse results, particularly for directions lying so close to each other that it is impossible to observe differences between spectra (in the limit of both low experimental statistics and resolution). Owing to this, we suggest measurements of 15-SDs (but a smaller number, e.g. 10- or even 7-SDs (see Fig. 2 in Ref. [16]) can be ok). This applies in particular to those materials where the isotropic core has an incomparably higher contribution than the valence electrons, and the statistical precision of the anisotropic valence contribution needs to be carefully considered.

i	(Θ_i, ϕ_i)	w_i	Miller	(Θ_i, ϕ_i)	w_i
1	(79.011 , 11.299)	0.28379	[5 1 1]	(78.904 , 11.310)	0.28419
2	(64.494 , 35.344	0.25037	[17 12 10]	(64.333 , 35.218)	0.23913
3	(80.997 , 33.679)	0.46584	[15 10 3]	(80.552 , 33.690)	0.47668

Table 1: Spherical coordinates (Θ_i, ϕ_i) of 3-SDs displayed in Fig. 1 with the corresponding weights to describe the isotropic function. The three last columns show coordinates and weights if the 3-SDs were described using Cartesian vectors which are the Miller indices of the directions.

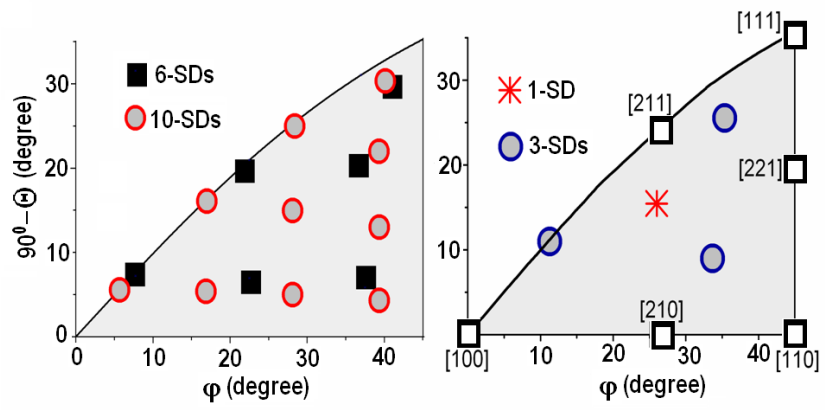

Figure 1: Stereogram of nonequivalent directions in the BZ for cubic structures. Left part: 6- and 10-SDs; right part: 1- and 3-SDs and 6 directions (marked by open squares) proposed by Betts *et al.* [8] and used in [1].

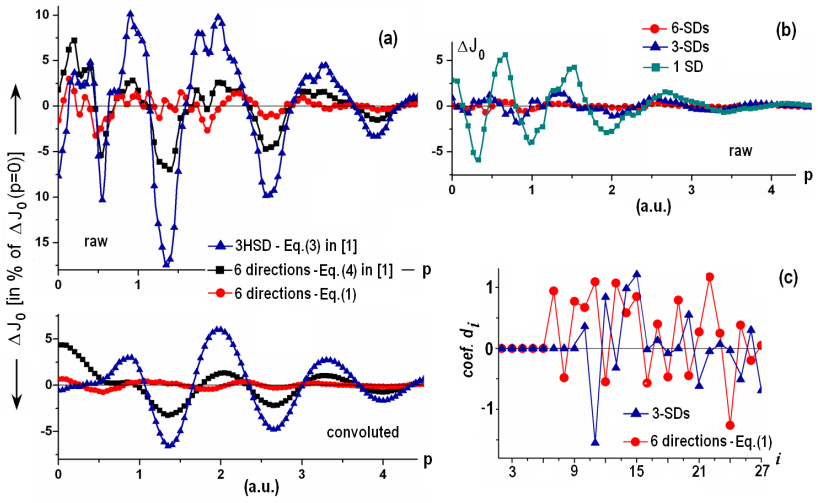

Figure 2: Differences between isotropic $J_0(p)$ estimated from magnetic Compton profiles $J(p_z)$ along 15-SDs and along five sets of sampling directions displayed in Fig. 1. The area under $J_0(p)$ should be normalised to the spin magnetic moment, but that has not been done here. For the 6 directions marked by the open squares in Fig. 1, we used weights from Eq.(4) in Ref. [1] and a correct set of weights (Eq. (1) in this paper). $J_0(p)$ is given in a %-ages of $J_0(0)$. Part (c) presents values of d coefficients, which define the deviation of the approximated $J_0(p)$ from its true value for successive harmonics i (see Eq.(4) in Ref. [7]), shown for 3-SDs and six sampling directions (Eq. 1 in this paper).

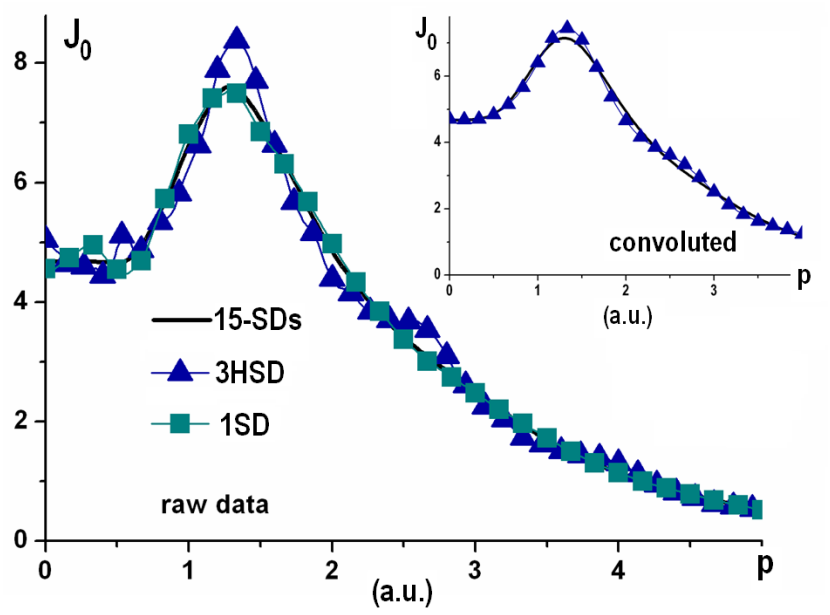

Figure 3: Isotropic $J_0(p)$ magnetic Compton profile calculated from 15-SDs (solid line), 3 HSDs (triangles) and a single special direction (1SD, squares). After convolution with the experimental resolution, 1-SD describes $J_0(p)$ very well.

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[15] For cubic systems, the choice of 1-SD is unequivocal, with all authors (e.g. [9, 11]) proposing the same solution, namely the intersection of the zeros lines of the first two anisotropic cubic harmonics F_4 and F_6. They intersect at a single point with coordinates $(\Theta, \phi) = (74.53560^\circ, 26.00130^\circ)$. In this respect the cubic structures are unique, because along one particular special direction contributions coming from the two first anisotropic components (with $l = 4$ and $l = 6$) are equal to zero. For all other structures, 1-SD allows the elimination of only the contribution from one component with $l = 2$. The single special direction is $\Theta = 54.7356^\circ$ and $\phi = 15^\circ, 22.5^\circ, 30^\circ$ for the

hcp, tetragonal and trigonal structures, respectively. For cubic structures the anisotropic component with $l = 2$ does not exist due to the existence of the three 4-fold axes.

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