# *Antiferromagnets, Shull peaks and Net Plant Angles*

outlined by Dr John S Plant, November 2022

[ further notes and references at https://plant.one-name.net/jsp.html#physics ]

In 1994, two Americans received a Nobel Prize for some neutron scattering techniques, one was Clifford Shull for uncovering antiferromagnetic peaks of diffraction. A few years later in 1999, George E Bacon received the gold medal for Experimental Physics from the Institute for Physics, at a time when there were still only two such gold medals, the other being for theory. Bacon's medal was for contributions to Neutron Diffraction, consistent with his having been the first to carry out such experiments outside of the USA, following on from his work on both radar and nuclear during the war. When computers were still rare, studying under George Bacon for my PhD, I wrote a computer program in 1967 for calculating model values for Bragg-Bacon neutron diffraction intensities, including ways of assessing models for antiferromagnetic structures via the Bacon intensities of the Shull diffraction peaks.

Diffracted peaks of neutron intensity arise from the nuclei of structurally arranged atoms and, also, in the case of an antiferromagnetic structure, from unpaired electron spins or orbitals in moment-bearing magnetic atoms. A favoured technique involves the diffraction from powdered crystalline solids, though sometimes larger single crystals are advantageous. My computer program of 1967 allowed relevant parameters to be derived as weighted-least-squares fits to the observed intensities from crystalline powders, with the powdering helping by averaging all orientations of the crystalline structure [Chapter 2 and Appendices II and III, JSP-PhDthesis-1970]. Being attached to GEB at Sheffield University and based at the AERE Harwell Laboratory near Oxford, I obtained the said diffraction peaks for various metallic alloys, along with careful measurements of their intensities; Bacon was known for his careful experimental studies in place of sometimes rushed and wrong results. Though not now appreciated as remarkable, I also had access to rare computer facilities at AERE Harwell.

***An unexpected inclination of a spin-direction axis*:**
In particular, my computations of structural models for antiferromagnets included a parameter for the magnetic spin inclination to a unique symmetry axis, as occurs in certain crystallographic structures [JSP-PhD-1970 pp. A8 and A11]. The computations gave rise to a value of slightly less that 70° for this inclination in the tetragonal crystallographic lattice of metallic AuMn. This same value was retained throughout several alloy series with substituted non-magnetic atoms such as Zn to dilute the Mn. This constant spin inclination, as fitted to the observed intensity results, differed at 70° from the previously supposed 90° for this $t_1$ phase of AuMn. In other words, it had previously been assumed that that the spins had been aligned in the crystal structure's basal plane, which was at right angles to the unique tetragonal c-axis, and for example it could be presumed to lie along one or other of this basal plane's two principal a-axes. This freedom of choice, of which of the two a-axes, could be envisaged to be for two different types of antiferromagnetic domain, each having their spin-direction axis along one or other of the two a-axes. Such domains in an antiferromagnet, as opposed to a ferromagnet, were relatively speculative, with some proposing more exotic super-positions of components of magnetic structure, without their separation into separate domains, which could be favoured for instance to apply in a slightly different antiferromagnetic $t_2$ phase of AuMn.

Subsequently, I used an acronym FFD-UND to label this powder-diffraction method of studying antiferromagnetic structures [Form-Factor Dependent – Unpolarised Neutron Diffraction] with a view to enhancing it with further types of neutron study. The word 'dependent' of this acronym arises because the magnetically diffracted intensities depend on a form-factor representing the electronic state of the Mn atoms; that substantially confounds a sure and precise evaluation of the net-spin-direction axis along which opposing spins, distributed throughout the antiferromagnetic structure, are aligned. For a metal, the unpaired spins for the form factor could likely be in the 3d-shell, for Mn, but this could be affected also by 4s-shell electrons or others that the metallic conduction implies. For my 70° instead of 90° result for the $t_1$ spin-direction axis, I had relied on a measured form factor that had been determined

by experiment for an inorganic compound, which could more confidently be assumed to have a $Mn^{2+}$ state. As a further discrepancy for AuMn, an additional parameter that I determined for the atomic-spin-moment was $4.6\mu_B$ instead of the theoretical $5\mu_B$ expected for unperturbed $Mn^{2+}$; this value also differed from a previous $4.2\mu_B$ that had been deduced with the 90° assumption for the spin-direction axis of AuMn.

***Extending to an NPA method*:**

To delve deeper into these deviations from a simple model, I envisaged a Neutron Polarisation Method, which I termed FFI-NPA [Form-Factor *Insensitive* – Neutron Polarisation Analysis] since this method was less dependent on the form factor, apart from the possibility of form-factor anisotropy. Following my three years at Harwell and then a three-year Post Doctoral Fellowship in Australia (1970-73), I sought to apply this untried approach to a large single-crystal of $t_1$ AuMn grown for me at Monash University in 1971; this had in fact been for my inelastic neutron scattering experiments on AuMn at Lucas Heights near Sydney [I eventually found time to publish these inelastic and some other investigations of AuMn as JSP-JPhysF-1979]. For the FFI-NPA experiment in 1975, I obtained access to neutron beam time, with a need only for a small additional device, on a polarised-neutron triple-axis spectrometer D5 at the Institute Laue Langevin at Grenoble. In our general (GEB and JSP) Sheffield University report to the ILL, outlining our various results obtained there in 1975, I just noted, for the time being, my anomalous finding of 0.52, instead of 0.5, for the mid-line of a particular sinusoidal variation. This implied some misalignment or other 'imperfection' somewhere in the experiment; those responsible for the D5 instrument held that there was no such misalignment in the D5 apparatus.

As with my other results, publication was delayed after my return to England in late 1975, due to other commitments, along with working through the considerable backlog of the experimental results that I had accumulated since 1967, at three different research facilities: AERE Harwell in England; Lucas Heights in Australia; and at the ILL in France. I eventually caught up with publishing my FFI-NPA results in 1981 [JSP-JPhysF-1981] and, subsequently in 1991, I reviewed a full range of associated neutron methodologies including especially my FFI-NPA enhancement for investigating $t_1$ AuMn [JSP-CrystallographyReviews-1991].

*Men of Achievement, Fifteenth Edition, 1993/94, International Biographical Centre, Cambridge, England (1992, Melrose Press, Bath)*

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*(eg. line 3 reads:* 2 s[ons] .. BSc [1st class] hons*)*

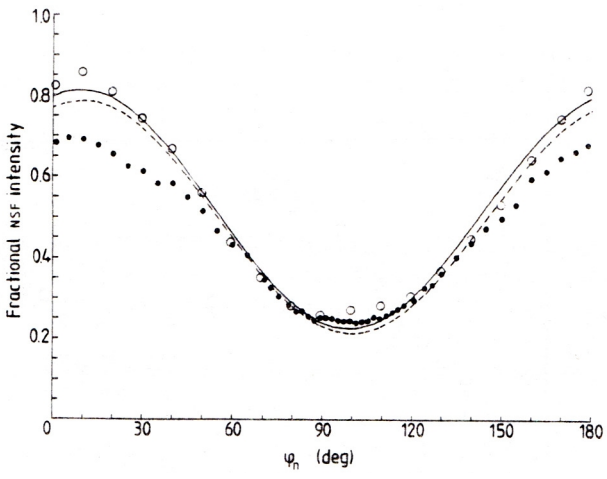
These FFI-NPA measurements involved considering projections of the net-spin-direction axis, associated with the Mn atoms, as planted onto certain diffraction planes. The opposing spin directions along the axis become slightly canted in a magnetic field, allowing some magnetic manipulation, to favour a spin-direction axis at right angles to the field. The diffraction planes I used for the planted projections were: first, onto the basal plane of the structure; and, secondly, on to a particular plane inclined at 65° away from the basal plane. The method included rotating the crystal around a full circle of angles in each of these two diffraction planes. Accordingly the abbreviation NPA, in the designation FFI-NPA, can be said to refer straightforwardly to a Neutron Polarisation Analysis instrument; or, it can imply instead the angles, within the respective planes, of a component of the net-spin-direction axis asplanted onto the chosen planes. More succinctly, this involved the Net Plant Angles of the spin-direction axis.

The abbreviation 'FFI-UND- NPA' in the extracted biographical note above can be described further as follows. Here UND- can refer to the aforesaid initial Unpolarised Neutron Diffraction experiment, though instead it can refer to the UND-result obtained from adding together both the spin-flip (SF) and non-spin-flip (NSF) neutron intensities, in an NPA experimental arrangement. The total SF+NSF intensity is largely uninformative – it can depend for example on the degree of neutron absorption or extinction in the studied crystalline sample. By separating the SF and NSF components of the neutron scattering and determining their fraction, more informative results emerge that are relatively form-factor-insensitive; this gives the extension of UND to the more informative UND-FFI- as denoted in my above biographical note. To emphasise that the SF and NSF intensities can be determined separately at a given Net Plant Angle, by means of Neutron Polarisation Analysis, this gives the addition of NPA in the designation UND-FFI- NPA.

***The NPA Results*:**

Specifically for $t_1$ AuMn, the results from the FFI-NPA experiment showed that the projected net-spin-direction axis, planted in the basal plane, gave the smallest NSF fraction of intensity at an NPA angle close to only *one* of that plane's two principal a-axes. This minimum occurs with only a small applied magnetic field, as needed to polarise the neutrons. When a large magnetic field is applied, the NSF fractional intensity falls twice in 180°, to minima at *both* of the two a-axes, separated by 90° – these can both be called 'easy directions' for the plant of the magnetic-spin axis. In other words, in a low polarising field, the net-spin-axis dip of NSF intensity was more predominantly near to one principal a-axis, explicable as an inequality between two types of antiferromagnetic domain, though a high field could force the dips to near both of the two basal-plane a-axes.

For the second investigated diffracting plane, it had one its axes lying along an a-axis and the other at right angles inclined at 25° away from the unique tetragonal c-axis. The NPA results for this plane are shown in the Figure below, which is taken from my paper JSP-JphysF-1981 in which a fuller set of results is included. This shows the fraction of the diffracted neutron intensity that is non-spin-flip (NSF) in a 360° NPA rotation, with some equivalent angles superimposed on the 180° scale at the bottom of the graph. An NPA rotation in this inclined plane can be expected to give an NSF fractional intensity varying from roughly 82% to 18%, if the spin-axis lies along an a-axis of the crystallographic structure.



The experimentally observed results, in the above figure, show something similar to that hypothetical model. However, for the high-field black dots, as well as the low-field open circles, the NSF fractional intensity does not fall fully to a single clear 'easy planted direction' near 100° on the scale; this angle on the scale corresponds roughly to the a-axis that is included in this inclined diffraction plane. A small but instructive detail is that the 'field-forced' black dots are spread evenly flat across 20° or so of breadth across the bottom of the dip, whereas the low-filed open circles show a preference for one side of this breadth. This can be explained by antiferromagnetic domains with 'easy planted directions' for the spin-axis at around 10° either side the included basal a-axis. For the field-forced result, there is more equality between the supposed domain types, each having a planted spin-direction axis in this inclined plane at one side or the other of the a-axis.

The neutron results overall for this AuMn crystal can be summarised as follows. Earlier, neutron diffraction rocking curves had indicated misalignments in the crystal structure of around ±1°, attributable to the martensitic twinning in fine strips within the large crystal. In addition, the aforementioned unexpected 0.52 value, instead of 0.5, in the basal-plane NPA investigation, can be explained by some $8^{\circ}$ misalignment in the experiment, if not a small imperfection in the degree of neutron polarisation. In my initiating FFD-UND [form factor dependent] powder results of 1967-70, the antiferromagnetic spin-axis could be considered, more liberally, to have been inclined out of the basal plane by 26° or 18° or 0° for a wider range of theoretically-supposed form-factors, based on the ionic states of $Mn^{+}$ or $Mn^{2+}$ or $Mn^{3+}$, with a maximum inclination of 32°. Whereas the initial analysis gave a reasonably surmised spin-axis at an ≈20° inclination out of the basal plane, the further experimentation indicated a qualitatively similar finding of roughly ≈±10° inclinations away from the a-axis in a plane inclined at 25° from the c-axis, to imply only a slightly different ≈±11° in the ac-plane, if that is where the spin-direction axis lies. The ac-plane itself is not available since it corresponds to zero neutron intensity from this antiferromagnetic structure.

As at November 2022, I still have the [001] stress-cooled 1cc crystal slab of $t_1$ AuMn though it is possible that the stress-cooling might have aged.

***The fuller context of neutron results*:**

By more straightforward experimental methods, the c-length of a unit cell of the crystal structure of AuMn is distorted from cubic in the $t_1$ phase to the extent of c/a~0.93 at 4.2°K. The $t_1$ antiferromagnetic phase extends up to a temperature of $T_N$~515°K in stoichiometric AuMn, though this falls with Mn dilution. In my assessed models for the magnetic exchange interactions, for the various alloy series, I took account of the changes in magnetic structure in those alloy series in which the Mn-Mn first- and third- neighbour interactions diminish by lack of Mn population in a structurally ordered manner; together the alloy series suggest, most simply, a strong negative interaction between 'third-nearest' neighbour Mn atoms. These 'third-neighbour' interactions can be visualised as between Mn atoms at opposite diagonal corners of a structural cell, mediated by an intervening Au atom at the cell's body centre. Given that the powder UND spin-direction-axis inclination out of the basal plane remains constant throughout random or ordered dilutions of the Mn lattice, it might be considered as at least a possibility that the initially-unexpected spin-axis inclination could involve an indirect influence from the unpaired electron of the intervening Au.

In the $t_1$ phase of AuMn, the investigated spin-direction reverses in successive planes normal to the c-axis. This reversal at the atomic level means the spins cancel out at larger distances, hence bulk antiferromagnetism. Instead of a strong negative 'third-neighbour' Mn-Mn interaction, I also considered the possibility of fully anisotropic Mn 3d-orbitals with the 'first-neighbour' interaction strongly negative along the c-axis, unlike its counterparts along the two a-axes. This is less elegant however for the $t_2$ phase of AuMn, in which the spin-direction reverses along one or other of the two a-axes (in this $t_2$ phase, the lattice distortion is c/a>1 instead of c/a<1). In a quest for more elegant symmetry for $t_2$ AuMn, a superposition can be considered of a reversal along both of the basal a-axes. Such tidying does not tidy away, however, the inclined spin-axis evidenced for $t_1$ AuMn.

***References***:

*JSP-PhD-1970*: J S Plant, 'Neutron Diffraction Studies of the Relationship between the Magnetic andbles Chemical Structures of some Manganese alloys', PhD Thesis, University of Sheffield, 1970.

*JSP-JPhysF-1979*: J S Plant (1979) ‘Magnetic order and coupling in Heusler alloys $Au_2(Mn, Z)_2$’, Journal of Physics F: Metal Physics, Vol.9, pp 545-556.

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*JSP-CrysRev-1991*: J S Plant (1991) ‘An Enhanced Methodology for Antiferromagnetic Structure and Form-factor Determinations', Vol.2, pp 205-233.

Also: https://plant.one-name.net/jsp.html#physics