RIETVELD REFINEMENT OF MAGNETIC STRUCTURES FROM PULSED-NEUTRON-SOURCE POWDER-DIFFRACTION DATA.

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Abstract

The General Structure Analysis System, GSAS, has recently been modified to include magnetic neutron-scattering cross-sections. Low-temperature diffraction data have been taken on the hexagonal noncollinear antiferromagnet UPdSn on both the HIPD and the NPD powder diffractometers at LANSCE. The low-resolution data reveal that the magnetic structure has orthorhombic symmetry (magnetic space group $P_{C}m'c2_1$) between 25K and 40K, and monoclinic symmetry (magnetic space group $P_{C}112_1$) below 25K. The high-resolution data reveal that there are structural distortions with corresponding symmetry changes in each of these phases, to give chemical space groups $Cmc2_1$ and $P2_1$ respectively, while the paramagnetic phase above 40K has space group $P6_3mc$. Using GSAS, we have refined data sets from both diffractometers simultaneously, including both magnetic and structural cross-sections. Magnetoelastic coefficients for the distortions have been extracted and we have determined the sign of the coupling between the structural monoclinicity and the magnetic monoclinicity. The magnetic results from Rietveld refinement are in good agreement with model fitting to the integrated intensities of seven independent magnetic reflections and these, in turn, agree with measurements made on the same sample using the constant-wavelength reactor technique. Our results therefore validate, to some level, both the technique of using spallation sources for complicated magnetic structures and the specifics of the GSAS Rietveld code.

1. Introduction

The main impact of pulsed spallation neutron sources in the field of crystallography has been in performing high-resolution structural studies. On the other hand, there has until recently been relatively little work at spallation sources on the solution of magnetic structures, a traditional domain of reactors. There are several reasons for this dichotomy. Firstly, while high-resolution studies can be performed with good intensity in backscattering (as is very effective for structural crystallography), the backscattering geometry is of less use for magnetic problems because it forces one to use excessively long neutron wavelengths. Secondly, there has been concern that the wavelength-dependent corrections for absorption and extinction cannot be made reliably. In this article, we will demonstrate that magnetic powder diffraction can be done equally well at the present generation of spallation sources and reactors and that the former are particularly effective for the studying previously undetermined magnetic structures and the interplay between magnetism and structure. A useful tool in this field is the Rietveld refinement program GSAS[1], which now allows simultaneous refinement of data from multiple phases taken instruments with different resolutions and including magnetic cross-sections. We have validated the program for the particular case of the noncollinear hexagonal antiferromagnet UPdSn[2], on which we have data from the same sample taken on both of the LANSCE powder diffractometers as well as the BT-9 constant-wavelength machine at NIST. Not only do we get the same results at reactor and spallation source, but GSAS also gives the same quantitative results as the traditional method of fitting integrated intensities from individual reflections to the magnetic model.

2. Magnetic Rietveld Refinement for Spallation Source Data

Initially, magnetic diffraction data taken on the HIPD powder diffractometer[4,5] was handled by individual peak fitting using the program FIT_PEAKS[6]. This uses the same lineshape description as GSAS and corrects for the incident spectrum variation in the same manner, but does not allow explicitly for the variation of absorption or extinction with wavelength. The integrated intensities are then fitted to a model using a purpose-written program. This has been

done in various cases, including noncollinear antiferromagnetism in the case of UPdSn[2], large-cell collinear antiferromagnetism in the case of UNiGa[7] and an incommensurate structure in the case of UPtGe[8].

But calculation of magnetic diffraction intensity from commensurate magnetic structures is now explicitly included in GSAS[3]. Magnetic structures can be tackled either as an extra purely magnetic phase, or as a phase that gives both nuclear and magnetic intensity. In either case, GSAS handles the magnetic symmetry in terms of the magnetic Shubnikov space groups, which are supergroups of the regular crystallographic space groups. The magnetic space group is specified by taking the normal space group and turning on the "colours" of any combination of basis symmetry operators that define the crystallographic space group. While one uses the normal space-group section of GSAS to determine which phases are magnetic, the coloured symmetry elements are turned on or off in the atom-editing section of the least-squares option. GSAS then determines automatically the constraints on the moments imposed by the group. On the other hand, the systematic absences (as used in the reflection generator POWPREF) are calculated by a numerical sampling method. Finally, one needs a magnetic form factor and this is parameterised in the following way:

$$F(Q) = \sum_i a_i e^{-b_i Q^2} + C$$

(1)

where the a_i, b_i and C are constants, that can be fitted in GSAS to published experimental or theoretical form factors in the form of a user-provided data file, and $Q = \sin\theta/\lambda$. This is handled within the form-factor section of the least-squares option within GSAS.

3. Results

The material that we have studied most extensively is the noncollinear hexagonal antiferromagnet UPdSn. We have now studied the same powdered sample on HIPD, NPD and on the BT-9 triple-axis spectrometer (in two-axis mode) at NIST[2,9,10]. Our original powder diffraction data are shown in Figure 1, and from these we were able to solve unambiguously the magnetic structures in the two magnetic phases. In addition, we determined that the Pd and Sn atoms are chemically ordered, in contrast to other isostructural compounds. In the subsequent reactor study[9] of the temperature dependence of the order parameters, we showed that we get the same results, both for the integrated intensities of individual reflections and for the parameters in the magnetic model. While this may sound a trivial matter, at that date nobody had demonstrated that this was the case and the prevailing wisdom was that spallation sources were somehow unsuited for magnetic studies. In any case, the Lorentz factors L are completely different for the two types of experiment:

$$L \propto \lambda^4 \text{ for time-of-flight; } L \propto \frac{1}{\sin\theta \sin 2\theta} \text{ for constant wavelength}$$

(2)

and in addition, the spallation source data are divided by the incident spectrum. The fact that there is good agreement indicates that these corrections are being applied properly, out to d-spacings of 8Å and beyond.

Since then, we have also done a high-resolution study on NPD, our 32-m high-resolution powder diffractometer[4], and have observed magnetically driven structural distortions. Fig. 2 shows the orthorhomic and monoclinic splittings of the 110 hexagonal reflection. These new data have been used in a Rietveld refinement together with the older low-resolution data from HIPD. While the NPD data are best for observing the structural distortion, the HIPD data are best for observing magnetism. The resultant low-temperature structure is shown in Fig. 3. In these refinements, it is even possible to determine the sign of the coupling between "magnetic monoclinicity" and "structural monoclinicity", that is whether the projected moments prefer to point across the short diagonal of the monoclinic cell or across the longer diagonal. In some

sense, these are determined independently, the magnetic monoclinicity being proportional to the amplitude of the 010 magnetic reflection, while the structural monoclinicity is primarily determined by splittings like those in Figure 2. The 120 reflection is particularly sensitive to this coupling constant, and portions of data from the +90° bank of HIPD are shown in Figure 4. The model with moments pointing across the short diagonal is clearly preferred. The Rietveld refinement included ten independent banks of data (four from NPD and six from HIPD, with parameters given in Table 1) including magnetism. At the lowest temperature, we used the crystallographic space group $C112_1$ (in the double-sized magnetic unit cell equivalent to $P2_1$) and magnetic space group P_C112_1.

4. Comparison with Reactors

We have conducted our program both at LANSCE and at the NIST reactor. With the technology presently in service, the spallation source is clearly superior for powders with unknown magnetic structures and for problems in which there are also structural concerns. Having solved the magnetic structure, one often wants to look at the intensity of a particular reflection in detail as a function of temperature, magnetic field and history. In this case the resolution can be relaxed with no loss of information, and we typically perform such measurements on a single-detector two-axis reactor diffractometer with relaxed collimation. So our philosophy is like that in other areas of neutron scattering: the broad survey work is better done at the spallation source, whereas the details are better examined at a reactor.

Of the machines currently in service, the "banana-detector" diffractometers D1B and D20 at the ILL probably have the highest total data rates of any powder diffractometers, and as comparable samples of Bi_2CuO_4 have been studied[11,12] on both HIPD at LANSCE and on D1B at ILL, we have made a comparison of data rates on the two machines[13]. The basis of our comparison is the intensity of the lowest order 100 magnetic reflection at d = 8.5Å. The 40° banks of HIPD have higher resolution (1.76% rather than 2.8%) and the signal-to-noise ratio is 8 times better on HIPD. But, even after correcting for the resolution difference (assuming the intensity is proportional to the square of the resolution), D1B has a count rate 60 times greater than that of HIPD! So, present-day spallation source diffractometers are not competitive on intensity, for low-resolution magnetic studies, with the best reactor diffractometers.

There are however several easy ways to make up this difference. Firstly, our measurements were made at a current of 58μA and LANSCE's design current is 100μA. Secondly, D1B has a solid angle five times that of our 40° detector banks. From an engineering point of view it would not be very difficult to increase the area of our banks by an order of magnitude, as we currently only use one sixteenth of the available Debye-Scherrer ring. Finally, we are using 5.8Å neutrons to observe the 100 reflection on HIPD which has a water moderator. A liquid-methane moderator would give three times the flux at these wavelengths[14], with no significant degradation in resolution. In Figure 5 we sketch out the design of a diffractometer that would be suitable for such studies, as well as time-resolved structural diffraction and other high-intensity applications. Such a diffractometer could be built very easily and would be competitive on intensity with the best reactor diffractometers. As a bonus, the signal-to-noise ratio is likely to be significantly better and it will automatically collect higher resolution data at the same time, for free.

5. Conclusions

We have shown that magnetic powder diffraction can be done very effectively at pulsed spallation sources with the present generation of sources and we have demonstrated that we know how to make all the systematic corrections. We have also demonstrated that magnetic Rietveld refinements can be performed on spallation-source data and that one gets the same result as from fitting to integrated intensities from either spallation-source or reactor data. The pulsed source is particularly effective for cases where structure and magnetism are coupled or where the magnetic structures are previously undetermined.

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Table 1   Characteristics of detector banks on HIPD and NPD

Diffractometer (See Ref. 4)	Scattering angle (degrees)	$d_{max}(\text{Å})$	resolution $\Delta d/d(\%)$
NPD	±148	3.0	0.15
NPD	±90	4.0	0.25
HIPD	±153	4.8	0.7
HIPD	±90	6.6	1.1
HIPD	±40	13.0	1.8

Figure Captions

Figure 1.   Plot (from Ref. 2) of a portion of the raw data taken on a powdered sample of UPdSn in the +90° bank of HIPD at four temperatures: (a) at 13K in magnetic phase II which is monoclinic, (b) and (c) at 33.8 and 36.3K respectively in magnetic phase I which is orthorhombic and (d) at 46K in the paramagnetic hexagonal phase. The indices in the upper panel are for the magnetic reflections only, assuming the cell shown in Figure 3. The intensities have been divided by the incident spectrum.

Figure 2.   Plots (from Ref. 10) of the 110 hexagonal reflection in UPdSn as a function of temperature, taken on the +148° bank of NPD. The splittings have been indexed in the orthorhombic system at 32K and in the monoclinic system below that. The intensities have been divided by the incident spectrum.

Figure 3.   The crystallographic and magnetic structures at low temperature of UPdSn, with magnetic space group P_C112_1. The right-hand figure shows the monoclinic basal plane. The primitive crystallographic unit cell (which corresponds to the parent hexagonal cell) is shown by the dashed lines, while the magnetic unit cell is shown by the solid lines. The left-hand figure shows the projection onto a plane perpendicular to the a-axis. Neither the atom sizes nor the lattice constants are drawn to scale and the deviation from 90° of the monoclinic angle γ has been grossly exaggerated. However, the atom coordinates within the cell are drawn to scale.

Figure 4.   Plots (from Ref. 10) of a portion of the time-of-flight spectra, along with Rietveld fits, reflection markers and residuals, from one 90° bank of HIPD at 13K. The data in (a) and (b) are identical, but the refinements differ in that the x-component of the uranium moment μ_x has opposite sign, as shown in the insets. Each inset shows a schematic of the projection onto the monoclinic basal plane, as in the right-hand part of Figure 3. Note that the "positively-correlated" model shown in (a) is clearly preferred by the data. The intensities have been divided by the incident spectrum.

Figure 5.   Schematic diagram of the proposed next-generation high-intensity powder diffractometer suitable for magnetic diffraction studies, along with time-resolved and kinetic experiments.

Intensity vs. d-Spacing/Å plots at four temperatures: 13K, 33.8K, 36.3K, and 46K.

Peak labels (13K panel): 102, 120, 012, 101, 100, 011, 010

Liquid methane moderator

140°-150° detector

L_i=10m

Sample

30° - 40° detector

90° detector

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