Model-Free Polarized Neutron Diffraction Study of an Acentric Crystal: Metamagnetic UCoAl

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For the first time, a model-free procedure is developed to analyze polarized neutron diffraction data pertaining to acentric crystals. It consists of a two-step process, featuring first an effective flipping ratio and second a linear inverse problem. The latter is solved either by a new generalized inverse Fourier transform or by using maximum entropy. Using metamagnetic UCoAl as a test case, we find the following results: (i) the U and Co(2) moments increase with an applied magnetic field whereas the Co(1) moment remains almost constant; (ii) the U and Co(2) magnetic densities are weakly anisotropic.

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Polarized neutron diffraction (PND) [1] is the technique of choice to determine magnetization densities in magnetic compounds at a microscopic level. In a vast majority of cases, PND is used to study ferromagnetic moments induced by a large externally applied magnetic field. The physical information resulting from PND experiments is connected with the local magnetic susceptibility, shedding light on the magnetic density details pertaining to a single ion, or on the separate response of each localized magnetic center (e.g., high-T_c superconductors), or else on the chemical bonding or the free radical behavior at the molecular level (e.g., molecular magnets).

Since the pioneering work by Nathans *et al.* [2], PND has enlarged its scope with the availability of large magnetic fields, high-flux neutron reactors, and most recently, the use of maximum entropy in PND data analysis. Three benefits result from the use of the latter when a model-free approach is sought: (i) an enormous increase of resolution [3], resulting in (ii) the possibility to reconstruct 3D densities [4], and (iii) improved reconstructed 2D projections using all available 3D data [5].

But a link is still missing, and it is the purpose of this Letter to fill this gap for the first time: how to tackle *noncentrosymmetric* structures, which have been carefully avoided up to now except for a fistful of cases [6].

This Letter is divided into three parts. In the first one, we generalize the inverse cosine Fourier to the general acentric case (within a restriction to be discussed later), whereas in the second, we describe the alternate and much more powerful use of maximum entropy. In the third, we demonstrate in a real data case pertaining to the (111) uranium compound UCoAl how our new procedure discloses new physical results. The latter are compatible with a multipolar refinement *à la* Varghese and Mason [7].

For the sake of simplicity, only the following simple case will be considered hereafter. The sought magnetization density $m(\mathbf{r})$ at any $\mathbf{r}$ in the unit cell is collinear and parallel to a known direction $\mathbf{u}$, resulting in a scalar problem. Thus there is no ordered perpendicular component [8]. The polarization $\mathbf{P}$ of the neutron beam is assumed to be perfect ($P=1$). More elaborate corrections, although amendable, fall outside the scope of this Letter. We now introduce the following notations. Let $\mathbf{K}=K\mathbf{k}$ the scattering vector associated with a given Bragg peak hkl, $N(\mathbf{K})$ and $M(\mathbf{K})$ the related nuclear and magnetic structure factors. The K dependence will be skipped when possible for the sake of clarity. Let $\mathbf{M}=M\mathbf{u}$, $M=M'+iM''$, $N=N'+iN''$, $X=X'+iX''$, and $X^*=X'-iX''$ for any X. Finally, we introduce the two geometrical factors $q^2=1-(\mathbf{u}\cdot\mathbf{k})^2$ and $q'^2=\mathbf{P}\cdot\mathbf{u}-(\mathbf{P}\cdot\mathbf{k})(\mathbf{u}\cdot\mathbf{k})$ and let $R(\mathbf{K})$ be the flipping ratio, which is equal to

$$R=\frac{NN^*+q^2MM^*+q'^2(NM^*+N^*M)}{NN^*+q^2MM^*-q'^2(NM^*+N^*M)}, \tag{1}$$

and $\sigma(\mathbf{K})$ the related experimental error bar.

Our goal is to infer the best density $m(\mathbf{r})$ given a limited measured data set of flipping ratios. The N's, q^2's, and q'^2's are known.

The first step is to reduce the data to a set of unique reflections. The second one is to separate the reflections into two subsets: (i) the centrosymmetric reflections (for which N'' and M'' are zero) and the (ii) acentric ones. Starting with the first subset, it results from (1) that for a given $\mathbf{K}$, $M=M'$ obeys a quadratic equation. Most often, only one solution makes physical sense, and we shall assume this to be true in the remainder of this Letter. We then define an *exact* effective flipping ratio:

$$R_{\text{eff}}^{\text{centro}}=1+4q'^2\frac{M'}{N'}. \tag{2}$$

A related effective error bar σ_{eff} can also be introduced using the law of propagation of errors. In the case of a centrosymmetric crystal, the effective R_{eff} is defined as M, which is the related cosine Fourier component of the sought magnetization density $m(\mathbf{r})$.

The fundamental difficulty which arises for the acentric subset stems from intricate coupling between M' and M''

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resulting from (1), rather than from a nonvanishing M''. The crux of our suggested procedure is to define an *approximate* effective flipping ratio:

$$R_{\mathrm{eff}}^{\mathrm{acen}} = 1 + 4q'^2(\alpha' M' + \alpha'' M'') , \tag{3}$$

where $\alpha'(\mathbf{K})$ and $\alpha''(\mathbf{K})$ are known. One readily finds

$$\alpha' = \frac{N'}{N'^2 + N''^2} , \quad \alpha'' = \frac{N''}{N'^2 + N''^2} , \tag{4}$$

which generalizes the case of a centrosymmetric reflection.

In this form, R_{eff} becomes a linear functional of $m(\mathbf{r})$, and M' and M'' are now suitably decoupled. The reduction of R to such an R_{eff} entails the only serious limitation to our proposed procedure: *An acentric reflection* $\mathbf{K}$ *can be kept in the data set only if* $|M(\mathbf{K})| \ll |N(\mathbf{K})|$, *so that R can be expanded in series. Otherwise, it must be ignored. In practice, we keep all the acentric measured flipping ratios within 0.6 and 1.4. The first neglected term is then of the order of 1%.*

Consequently, retrieving $m(\mathbf{r})$ from the data is tantamount to solving a hugly undetermined linear system of equations, which writes in matrix form,

$$\mathbf{Y}(\mathbf{K}) = \mathbf{A}(\mathbf{K},\mathbf{r}) \cdot \mathbf{X}(\mathbf{r}) , \tag{5a}$$

where the different matrix elements write

$$Y(\mathbf{K}) = R_{\mathrm{eff}}(\mathbf{K}) - 1, \quad X(\mathbf{r}) = m(\mathbf{r}) , \tag{5b}$$

and

$$A(\mathbf{K},\mathbf{r}) = 4q'^2(\mathbf{K}) \frac{N'(\mathbf{K}) \cos \mathbf{K}\mathbf{r} + N''(\mathbf{K}) \sin \mathbf{K}\mathbf{r}}{N'(\mathbf{K})N'(\mathbf{K}) + N''(\mathbf{K})N''(\mathbf{K})} \Delta , \tag{5c}$$

and where Δ is the pixel size resulting from the discretization of the cosine and sine Fourier integrals over the unit cell. Similarly to [3] and [9,10], the symmetry of $m(\mathbf{r})$ is automatically enforced by replacing the cosine and sine terms by suitable averages over the space group of the crystal.

One way to find a unique solution to (5a) is to add the extra requirement that $\mathbf{X}(\mathbf{r})$ should have the minimum possible least squares norm (MNLS) $\mathbf{X} \cdot \mathbf{X}$ [11]. The solution reads

$$\mathbf{X} = {}^t\mathbf{A} \cdot [\mathbf{A}\,{}^t\mathbf{A}]^{-1} \cdot \mathbf{Y} , \tag{6}$$

where ${}^t\mathbf{A}$ is the transpose of $\mathbf{A}$. Finally, one obtains

$$m(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}} \frac{g}{g(\mathbf{K})} \frac{N' \overline{\cos \mathbf{K}\mathbf{r}} + N'' \overline{\sin \mathbf{K}\mathbf{r}}}{1 + \varepsilon(\mathbf{K})} \frac{R_{\mathrm{eff}}(\mathbf{K}) - 1}{2q'^2} ,$$

where V, g, $g(\mathbf{K})$, $\varepsilon(\mathbf{K})$, and $\overline{f(\mathbf{r})}$ stand for the volume of the unit cell, the order of the space group, a degeneracy factor, 1 for a centric reflection and 0 otherwise, and the average over the space group operations for any function $f(\mathbf{r})$, respectively. See [10] for a detailed similar case, which also features an extension incorporating experimental error bars. Notwithstanding the production of spurious correlation effects by the MNLS solution, the new explicit formula mentioned above remains useful to appreciate the largest features of the magnetization density $m(\mathbf{r})$. The detection of smaller effects requires the huge resolution enhancement resulting from the use of maximum entropy (MaxEnt) [12], for which our PND problem becomes a prototype once cast into (5a).

Extensive simulations were carried out to test both the MNLS and the MaxEnt procedures, from which the following conclusions emerge:

(i) Because our problem is linear, the use of Fourier differences generalizes straightforwardly to the use of effective flipping ratio differences, with the same benefits for both MNLS and MaxEnt. Because the signal-to-noise ratio decreases in the difference process and is crucial to MaxEnt, the relative benefit is less for this latter case.

(ii) The restriction of the acentric total data set to its centric subset can yield very wrong results when either a model-fitting, MNLS, or MaxEnt approach is used. By contrast, using the acentric subset alone produces much more satisfactory results, especially when MaxEnt is used. Some molecular crystals featuring free radicals show mostly acentric reflections (e.g., 85% for tempone and 96% for tempol). The related R values are all close to 1, making these compounds ideally suited for MaxEnt analyses despite very small centric subsets.

We now demonstrate the capabilities of our suggested procedures on a real system, metamagnetic UCoAl at $T = 5$ K [13], which we have selected since the magnetism of uranium and related compounds still arouses considerable interest [14]. The nuclear structure is characterized by the space group $P\bar{6}2m$, and the atoms lie either in the $Z = 0$ or the $Z = \frac{1}{2}$ section [Figs. 1(a) and 1(b)]. There are two nonequivalent Co sites, Co(1) and Co(2). Because of a very strong anisotropy, all the ordered magnetic moments are parallel to the $\mathbf{u} = \mathbf{c}$ crystal axis. We consider first a simulated and then two real data sets, corresponding to two distinct values of the magnetic field ($H = 1.7$ and 5 T). The set of Bragg peaks is identical for the three cases, corresponding to a complete set of flipping ratios for the $hk0$ and $hk1$ except for the 100, 600, 301, and 401 peaks, the nuclear structure factors of which are too small. Whereas Wulff *et al.* restricted themselves to the 11 unique centric reflections in [13], our present study takes 39 centric plus acentric reflections into account, some of which we remeasured in order to improve their statistical accuracy.

Because the spatial resolution is very poor along $\mathbf{c}$, projections along $\mathbf{c}$ must be considered rather than sections. Their retrieval remains a 3D process, the projection resulting from the sum over all sections [4,5].

In order to rate our MNLS and MaxEnt procedures, a first mock data set was generated by a preliminary U and Co monopolar refinement of the 5 T data. The calculated R_{eff} values were kept together with the experimental error bars. A second mock noiseless data set was generated by keeping 90% of the fitted uranium monopole contribution.

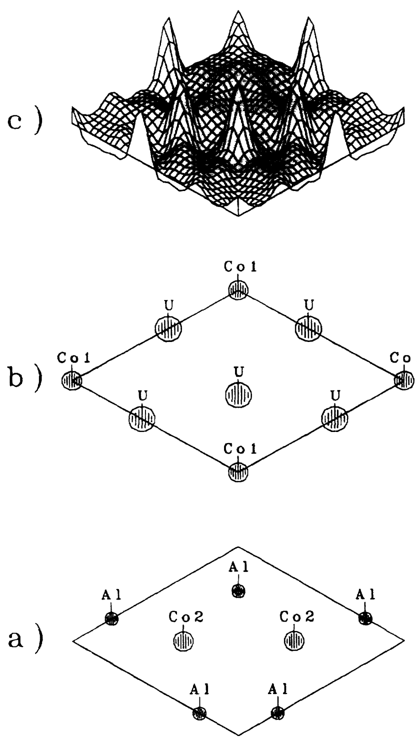

FIG. 1. (a),(b) Schematic sections of UCoAl corresponding to $Z=0$ and $Z=\frac{1}{2}$, respectively, and showing the locations of the atoms of the title compound. (c) Generalized inverse Fourier transform (minimum norm least squares) reconstruction of the projected magnetization density pertaining to the mock data set described in the text. Similarly to the difference-Fourier technique, part of the simulated U isotropic contribution ($0.330\mu_B$) was subtracted from a mock data set [U: $0.368\mu_B$, Co(1): $0.058\mu_B$, Co(2): $0.076\mu_B$] in order to reconstruct smaller features of a similar size. Note the absence of spurious splitting of the U peak, irrespective of the amount of the subtracted isotropic U contribution.

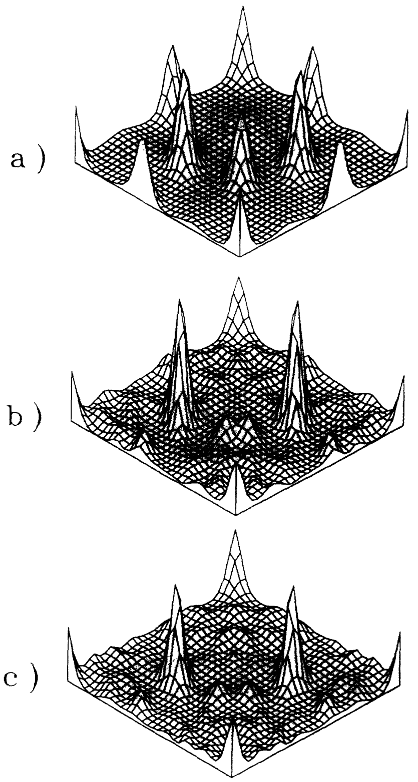

FIG. 2. (a) MaxEnt reconstruction counterpart of the MNLS solution displayed in Fig. 1(c) and pertaining to the same mock data set. (b) Difference MaxEnt reconstruction for the real data set at $H=5$ T. The fitted isotropic U contribution of $0.360\mu_B$ was subtracted from the first $R_{\rm eff}$ real data set. (c) Difference MaxEnt reconstruction for the real data set at $H=1.7$ T. The smaller fitted isotropic U contribution of $0.306\mu_B$ was subtracted from the second $R_{\rm eff}$ real data set. Note in particular the splitting of the residual U magnetic density, which directly demonstrates the related magnetic anisotropy.

We used the difference mock data set as our test case, thereby generalizing the Fourier difference procedure to eliminate truncation effects as much as possible. The 110 reflection was omitted because our acentric expansion is not valid in this instance, the related flipping ratio ($R\approx 1.9$) lying outside the [0.6,1.4] interval mentioned earlier. The MNLS solution, shown in Fig. 1(c), reveals the simulated Co moments nicely. Note the spurious truncation effect close to the Al site. The MaxEnt solution, displayed in Fig. 2(a), is much enhanced. The spurious remnant Al-like contribution sets the limit to our MaxEnt procedure: Our result is as good as our data (S/N ratio, **K** set) *and* our linear acentric approximation.

The above spectacular MaxEnt result prompted us to apply the same strategy to our two real data sets. The fitted monopolar uranium contribution was first subtracted from the real data, both for our 1.7 and 5 T data. The two ensuing MaxEnt projected magnetization density maps are shown in Figs. 2(b) and 2(c). Both the U and the Co(2) moments are found to increase with the magnetic field, and to be anisotropic: The equicontours of the Co(2) density (not shown) have a triangular shape and the peak of the U density is split. By contrast to the Co(2) moments, the Co(1) moments are found to be insensitive to the applied magnetic field and without a noticeable anisotropy. These results compare very well [15] with a U, Co(1), and Co(2) multipolar refinement using the standard MOLLY program adapted to refine on the $R_{\rm obs}-1$ values and to allow for possible magnetic deformations compatible with the crystallographic symmetry [16]. Note that the latter refinement alone is insufficient to conclude since (i) the resulting parameters are strongly correlated and (ii) the choice of the refined parameters is *ad hoc* and greatly conditions their values.

In summary, we propose two procedures to tackle the acentric PND case: MNLS and MaxEnt. We have applied them successfully to metamagnetic UCoAl and disclosed new physical results, substantiated by multipolar refinement: (i) the Co(1) and Co(2) are inequivalent ($\mu_{\mathrm{Co1}} < \mu_{\mathrm{Co2}}$) and (ii) U and Co(2) have anisotropic magnetic densities and increase with a magnetic field.

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