Magnetic Pair Distribution Function Software Development and Application to Manganese Telluride

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ABSTRACT

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The magnetic structure in certain thermoelectric materials has proven to be a relevant factor in their thermoelectric performance for technological application. A material's magnetic structure refers to the orientational correlations formed by the magnetic moments, which can either assemble into long-range patterns extending throughout macroscopic regions of the material, or short-range correlations that extend only over a few nanometers or shorter distances. These short-range correlations are often neglected in the analysis of these materials. However, it was recently realized that short-range magnetism can affect the performance of magnetic thermoelectrics, so it is important to include short-range correlations when studying magnetic structure. Analysis of magnetic pair distribution function (mPDF) data obtained from magnetic materials has provided a mechanism by which the short-range correlations can now be analyzed effectively. Manganese telluride doped with lithium and iron is one such material that has proven to be interesting, due to its magnetic and thermoelectric properties. This paper will cover improvements made to the software used for analysis of mPDF data, and the results of mPDF analysis of iron and lithium-doped manganese telluride.

Keywords: [manganese telluride, magnetic pair distribution function, thermoelectric]

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Chapter 1

Introduction

1.1 Short-range Magnetic Correlations in Thermoelectrics

Thermoelectrics are an exciting frontier of materials science for technological applications, having a wide range of uses, from harvesting energy from waste heat to providing solid-state cooling. Their low thermal conductivity juxtaposed by their high electric conductivity gives them a unique ability to convert heat energy to electricity at high efficiency. Candidate thermoelectrics can be found through an analysis of their atomic structure using modern methods such as x-ray and neutron diffraction, and their electric and thermal transport properties [1]. Recent developments show that magnetic effects can improve thermoelectric performance as well [2]. However, a problem arises when trying to determine the magnetic structure while using conventional methods such as standard neutron diffraction. At high temperatures, thermal energy can destroy long-range magnetic order, such that any magnetic correlations that remain are short-range, with a typical scale length of one nanometer. Unfortunately, standard analysis techniques for x-ray and neutron diffraction are only useful in determining the long-range order of structures, as short-range correlations are shown in diffuse scattering effects, which have much weaker intensity than the sharp Bragg peaks arising

from long-range correlations [3]. Because thermoelectrics often operate at high temperatures while in use, a different method must be used to determine their short-range magnetic order. This need has been addressed through the study and modeling of atomic and magnetic pair distribution function (PDF) data. The following sections address magnetic PDF (mPDF) analysis specifically, and the software used in this technique.

1.1.1 Magnetic Thermoelectrics

The effectiveness of a thermoelectric can be quantitatively described by the dimensionless thermoelectric figure of merit, zT, given by

$$zT = \frac{\sigma S^2 T}{\kappa}, \tag{1.1}$$

where σ represents the electrical conductivity of the material, S is the Seebeck coefficient or thermopower, T is the temperature of the material, and κ is the thermal conductivity. High-performance thermoelectrics typically have zT values around 1. An effect known as "magnon drag" was first discussed for magnetic thermoelectrics in 1964 [4], and it was shown to increase the value of zT, thus increasing the thermoelectric properties of certain magnetic materials [5]. These magnons, also known as spin waves because they are a propagating disturbance of the long-range magnetic ordering pattern, are thermal fluctuations of the magnetic ground state, and interact with electrons to increase electrical conductivity in metals. However, magnon drag only applies to materials with long-range magnetic order, and thus may not always be particularly helpful in thermoelectric applications. A similar effect, known as "paramagnon drag" proves to be much more useful, as it is present over shorter ranges when a material is in a paramagnetic state, thus proving to be a more useful application to our magnetic thermoelectric problem. The principle of paramagnon drag is the same as magnon drag, except that it applies to thermal fluctuations of a short-range ordered magnetic state in the paramagnetic phase of a material. Paramagnon drag was first discovered in manganese telluride [5].

1.2 Magnetic PDF Analysis

The magnetic pair distribution function (mPDF) of a magnetic material is generated through the Fourier transform of the neutron total scattering data obtained from a neutron diffraction experiment. The mPDF can be used to determine how the magnetic spins are oriented over nanometer length scales, a technique that was first derived in [2]. Because both the Bragg peaks originating from long-range order and the diffuse scattering arising from short-range order are included in the Fourier transform when generating the mPDF, it is sensitive to both the long-range and short-range magnetic correlations in the material, unlike conventional diffraction analysis methods. Therefore, mPDF analysis is useful for studying magnetic thermoelectrics where short-range magnetism is expected to be relevant. mPDF analysis also provides this information in real space, which gives data that is easier to visualize than diffraction data in reciprocal space. Software developed by Benjamin Frandsen allows the user to take real data and generate the mPDF, fitting the function to the real data. The software used in this technique will be covered more extensively in the next chapter.

1.3 Manganese Telluride

Manganese telluride is a particularly interesting candidate for a magnetic thermoelectric, and is the material being analyzed in this paper. It has a hexagonal crystal structure belonging to space group 194, and is an antiferromagnet below the Néel temperature of 307 K. The spins are aligned along the a-b plane and anti-aligned along the c-axis. It also has semiconductor transport properties with a band gap of 1.3 eV. Despite pure MnTe only having a zT value of 0.6, doping MnTe with other metals such as sodium and lithium increases zT to nearly 1, garnering interest in this material in the scientific community [6].

Other research groups are making efforts to find other dopants to pair with manganese telluride to enhance its thermoelectric properties. The particular sample used in the analysis below has been

doped with iron (Fe) in order to enhance its thermoelectric properties. The sample was synthesized by our collaborator Daryoosh Vashaee at North Carolina State University.

Chapter 2

Methods

This chapter will cover three main topics, neutron scattering and the mPDF technique, the software used to perform the mPDF analysis, and details about the mPDF measurements done on a sample of manganese telluride doped with lithium and iron.

2.1 Neutron Scattering

Neutron scattering is a method used in condensed matter physics to determine the structure and dynamics of materials. In this method, a neutron beam is fired into a sample. As the neutrons interact with the nuclei of the sample, they diffract, a phenomenon that occurs when a wave encounters an object of size comparable to the wave's wavelength. Diffraction from long-range structural order in crystals scatters the neutrons at specific angles according to Bragg's Law, resulting in sharp Bragg peaks. Short-range structural correlations result in diffuse scattering of the neutrons, for which the intensity is spread out over a broader range of scattering angles. Computing the Fourier transform of the total scattering pattern (referring to both the Bragg scattering and the diffuse scattering) produces the atomic pair distribution function (PDF), which provides information on where the atoms are located in the sample. The main advantage of generating the PDF is that the structural information is

transformed from momentum space (where the original scattering data is most naturally measured) into real space, which is much more intuitive to interpret and allows for easier modeling of the local structure [1].

2.1.1 mPDF

Neutron scattering can also be used to determine the magnetic structure of materials. Because neutrons are spin-1/2 particles, they can scatter as they interact with the magnetic moments resulting from unpaired electrons in the sample, providing data on the magnetic structure. Analogously to atomic PDF, the mPDF is obtained through a Fourier transform of the momentum space data obtained from the experiment to represent the magnetic correlations in real space. As with atomic PDF, this has the advantage of being easier to interpret and fit magnetic models compared to analysis of the momentum space data. [2]

2.2 Software Used in mPDF Analysis

2.2.1 Diffpy.mpdf Package

Diffpy.mpdf is a python package developed by Benjamin Frandsen for mPDF analysis [7]. Using the diffpy.mpdf package, a user can read in atomic structure data and calculate additional magnetic information. Important magnetic information includes the magnetic spins, the correlation length, a factor which indicates how likely two spins separated by a distance 'd' are to be correlated to each other, and the magnetic moments of the atoms. Using this additional information, the package can calculate the mPDF of the compound for comparison and fitting to experimental data.

2.2.2 Information Storage for diffpy.mpdf

How and where information about the magnetic structure is stored is a key part of any computer program intended to perform mPDF analysis. The atomic data is initially stored in a crystallographic information file (CIF file). A file containing the experimental data and relevant metadata associated with the experiment is produced by the bemaline computers during the experiment. The CIF file is then read into the diffpy.mpdf, and additional information regarding the magnetic structure is added by the user. However, at this point in the process, there is no functionality in diffpy.mpdf to save this additional information together with the original atomic data. Thus, the file format has been refactored to allow for easy storage and transportation at this stage. The next chapter will go into more details as to how this functionality was added.

2.3 mPDF Analysis on Manganese Telluride

Magnetic PDF data for manganese telluride was obtained from neutron scattering experiments conducted at the NOMAD beamline of the Spallation Neutron Source at Oak Ridge National Laboratory. The data received from the experiments is then read into a python script written in Jupyter Notebook, which first uses functionality from the diffpy.mpdf package to calculate the atom positions and spins of the MnTe sample, then producing the mPDF. Fits are then performed to see if the projections match up with the observed data. The fit variables include the spin orientation, the size of the magnetic moment, and the correlation length. These fits were conducted at the following temperatures, 120, 200, 250, 270, 280 290, 295, 300, 305, 310, 315, 320, 330, 350, 375, 425, and 500 K. Data for the following variables were recorded; the ’a’ and ’c’ values, which describe the unit cell of the hexagonal structure, the mPDF scale factor (related to the magnetic moment size), the angle of the magnetic spins from the c-axis ’theta’, and ’xi’ or the correlation length that was previously described.

Chapter 3

Results and Discussion

This chapter will discuss the results of the mPDF anlaysis of Li- and Fe-doped MnTe, and discuss the improvements made to the diffpy.mpdf package.

3.1 Software Updates Made to Diffpy.mpdf

One of the key features of diffpy.mpdf is creating a magnetic structure profile of a sample. However, once the magnetic structure is generated, there is no way to save the data. This gives rise to two main problems. First, once you use diffpy.mpdf to produce the additional magnetic information, it exists only in that python script, and in any future use the magnetic structure will need to be generated again. Second, if there are multiple collaborators on the same sample, the magnetic structure will need to be generated by both parties individually every time it needs to be used. This can give rise to inconsistencies and is generally inconvenient.

Thus, two main features were added to the functionality of diffpy.mpdf. The first is a save function, which allows the user to save the magnetic structure object to a text file. The code shown in Figure 3.1 shows code that gives two options for saving your object, one is a more thorough method that tracks all the variables that diffpy.mpdf adds and saves them into a readable text file.

```
def saveToFile(self, readable, filename):
    if readable==True:
        self.convToTxtFile(self, filename)
    else:
        self.pickleFile(self, filename)
```

Figure 3.1 Snapshot of the save function added to Diffpy.mpdf. The user can pass in a boolean "readable" to either save the magnetic structure in a readable text file or pickle the object into a smaller encrypted file. The user can then pass in a desired filename.

```
def pickleFile(self, filename):
    dbfile = open(filename, 'wb')
    pickle.dump(self, dbfile)
    dbfile.close()
```

Figure 3.2 Snapshot of the pickle function added to Diffpy.mpdf. This function is accessed when a user uses the save function and passes in a "false" value to the "readable" parameter. Shows the simplicity of this functionality.

The other possibility uses the pickle method, which serializes the Python object onto a relatively small data file. Figure 3.2 shows the simplicity of pickling the object, with the only drawback being that pickled file is serialized and not readable. The other functionality is a load option shown in Figure 3.3 that allows the user to load in a Python object from one of the saved files mentioned previously. This allows for users to save the new magnetic information created in the diffpy.mpdf package for later use. This also allows for easy transport amongst collaborators, as small files can be sent and then loaded using this functionality by another user.

```
def load(self, filename):
    if filename.endswith('.txt'):
        objData = self.readTxtFile(filename)
    else:
        dbfile = open(filename, 'rb')
        objData = pickle.load(dbfile)
    return objData
```

Figure 3.3 Snapshot of the load function added to Diffpy.mpdf. The user passes in the filename of the desired magnetic structure data. The function then determines the type of file passed in and either reads back in the readable text file and recreates the magnetic structure object, or unpickles the saved object and returns the original magnetic structure object.

3.2 Results of mPDF Analysis

The diffpy.mpdf software explicitly generates graphs containing the fitting of the generated mPDF to the observed data. Both Figure 3.4 and Figure 3.5 are two such plots, one at a lower temperature of 100 K and the other near the transition temperature at 315 K. The peaks show the atomic and magnetic correlations between atoms separated by a particular radial distances. The positive peaks refer to associations with the same atoms, whereas the negative peaks refer to associations with the different atoms in the sample. The fits describe the data well. The two figures clearly demonstrate that the fit projected from the derived mPDF is in line with the observed data. The most significant difference between the two figures is that the mPDF signal (gray and blue curves offset below the total PDF curve) is smaller and more heavily damped with r at 315 K (above the Néel temperature of 307 K) compared to 100 K. This proves that short-range magnetic correlations are present in the paramagnetic state in Li/Fe-doped MnTe, similar to those found in pure MnTe. Thus, paramagnon drag is still relevant for the Li/Fe-doped sample.

Additional information can be obtained from the mPDF fits. Figure 3.6 shows the angle the spins make with the c-axis at the different measured temperatures. As the material heats up, the spins

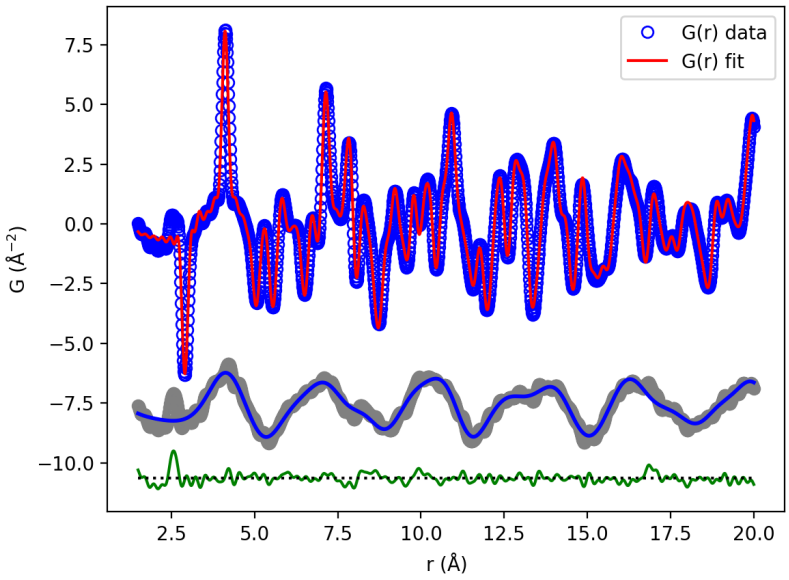

Figure 3.4 Magnetic PDF fit at 120 K. Both the atomic PDF and mPDF are shown. The blue circles represent the combined atomic and magnetic PDF obtained from the experiment. The red curve is the calculated total atomic and magnetic PDF. The gray curve offset below is the magnetic component of the data, and the blue line is the mPDF fit. Positive peaks show ferromagnetic pairs and the negative peaks show antiferromagnetic pairs. This fit shows that there are long-range magnetic correlations in the material at lower temperatures.

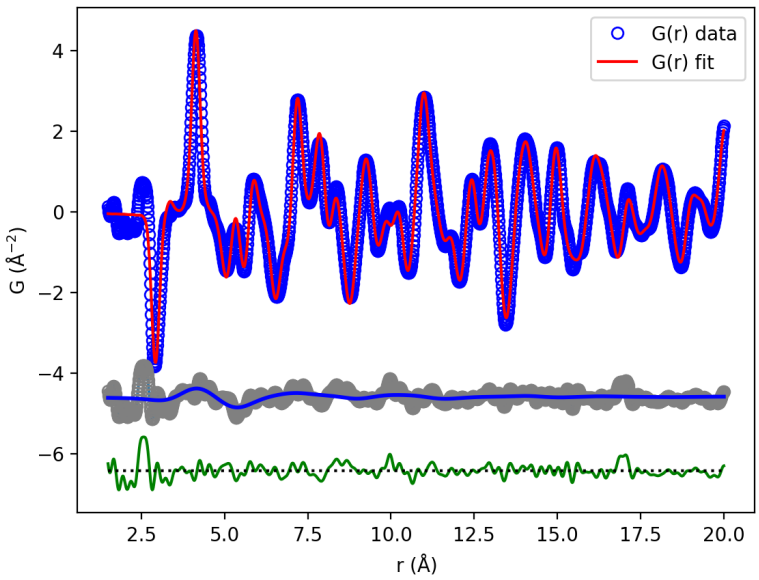

Figure 3.5 Like Figure 3.3, both the atomic PDF and mPDF are shown. The atomic correlations remain consistent at higher temperatures, but the magnetic correlations are less obvious, showing a much smoother curve. The consistency of the curve shows that the short-range correlations are still present.

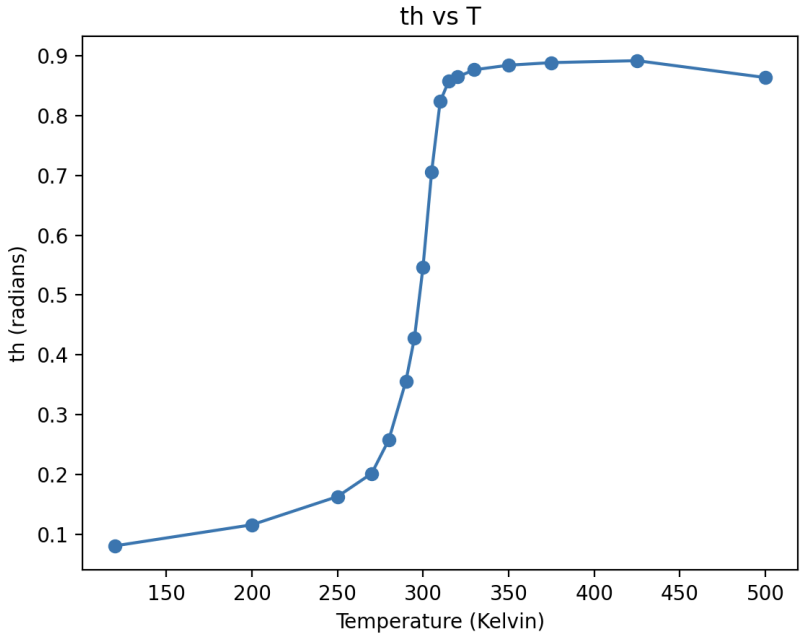

Figure 3.6 The average theta value from 1.5 $\mathring{A}$ to 20 $\mathring{A}$, or angle that the magnetic moment makes from the vertical c-axis, plotted at various temperatures. The steep climb shows the increased disorder as the material reaches and passes the transition temperature (307 K).

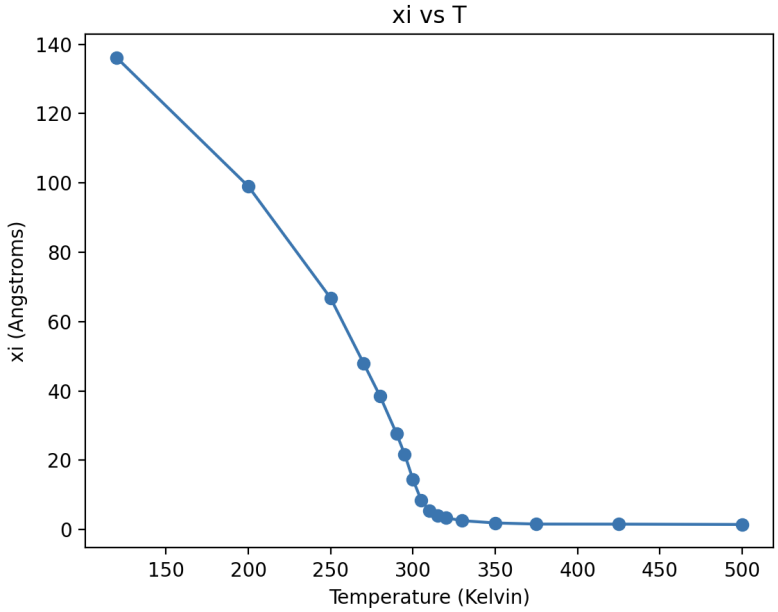

Figure 3.7 The xi values observed when analyzing the short-range correlations from 1.5 $\mathring{A}$ to 20 $\mathring{A}$ in MnTe plotted at the various recorded temperatures. The sharp dive in the correlation length shows the increased disorder as the transition temperature of 307 K is approached.

become less ordered and begin to wobble. This is especially obvious at the transition temperature, 307 K, where we see the largest increase in theta. This increased disorder is also visible in Figure 3.7, as the correlation length drastically increases as the temperature increases, showing that the material's spins become less ordered as its thermal energy increases.

These results provide valuable details about the magnetic correlations present in Li- and Fe-doped MnTe.

Bibliography

[1] S. J. L. Billinge and I. Levin, "The Problem with Determining Atomic Structure at the Nanoscale," Science **316,** 561–565 (2007).

[2] B. A. Frandsen, X. Yang, and S. J. L. Billinge, "Magnetic pair distribution function analysis of local magnetic correlations," Acta Crystallographica Section A Foundations and Advances **70,** 3–11 (2013).

[3] J. Bréger, N. Dupré, P. J. Chupas, P. L. Lee, T. Proffen, J. B. Parise, and C. P. Grey, "Short- and Long-Range Order in the Positive Electrode Material, $Li(NiMn)_0.5O_2$: A Joint X-ray and Neutron Diffraction, Pair Distribution Function Analysis and NMR Study," Journal of the American Chemical Society **127,** 7529–7537 (2005).

[4] J. Wasscher and C. Haas, "Contribution of magnon-drag to the thermoelectric power of antiferromagnetic Mn Te," Physics Letters **8,** 302–304 (1964).

[5] Y. Zheng *et al.*, "Paramagnon drag in high thermoelectric figure of merit Li-doped MnTe," Science Advances 5 (2019).

[6] W. Liu, X. Shi, M. Hong, L. Yang, R. Moshwan, Z.-G. Chen, and J. Zou, "Ag doping induced abnormal lattice thermal conductivity in Cu_2Se," Journal of Materials Chemistry C **6,** 13225–13231 (2018).

[7] B. A. Frandsen, H. K. Parker, J. A. Christensen, E. Stubben, and S. J. L. Billinge, "diffpy.mpdf: open-source software for magnetic pair distribution function analysis," **55,** 1377—1382 (2022).