Universidade de São Paulo
Instituto de Física

Propriedades Eletrônicas, Magnéticas e Estruturais do Candidato a Líquido de Spin $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$

Marli dos Reis Cantarino

Orientador: Prof. Dr. Fernando Assis Garcia

Dissertação de mestrado apresentada ao Instituto de Física
da Universidade de São Paulo, como requisito parcial para
a obtenção do título de Mestra em Ciências.

Banca Examinadora:

Prof. Dr. Fernando Assis Garcia - Orientador (IFUSP)

Profa. Dra. Letícia Mendonça Ferreira (UFABC)

Prof. Dr. Marcos de Abreu Avila (UFABC)

São Paulo
2019

FICHA CATALOGRÁFICA
Preparada pelo Serviço de Biblioteca e Informação
do Instituto de Física da Universidade de São Paulo

Cantarino, Marli dos Reis

Propriedades eletrônica, magnéticas e estruturais do candidato a líquido de spin $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ / Electronic, magnetic and structural properties of the spin liquid candidate $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. São Paulo, 2019.

Dissertação (Mestrado) – Universidade de São Paulo. Instituto de Física. Depto. de Física Aplicada.

Orientador: Prof. Dr. Fernando Assis Garcia
Área de Concentração: Fenômenos Magnéticos.

Unitermos: 1. Fenômenos magnéticos; 2. Física do estado sólido; 3. Mudança de fase.

USP/IF/SBI-016/2019

University of São Paulo
Physics Institute

Electronic, Magnetic and Structural Properties of the Spin Liquid Candidate $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$

Marli dos Reis Cantarino

Supervisor: Prof. Dr. Fernando Assis Garcia

Dissertation submitted to the Physics Institute of the University of São Paulo in partial fulfillment of the requirements for the degree of Master of Science.

Examining Committee:

Prof. Dr. Fernando Assis Garcia - Supervisor (IF-USP)

Prof. Dr. Letícia Mendonça Ferreira (UFABC)

Prof. Dr. Marcos de Abreu Avila (UFABC)

São Paulo
2019

Agradecimentos

Quero agradecer ao meu orientador Prof. Dr. Fernando Assis Garcia pela orientação do meu mestrado e desta dissertação, pelas horas desprendidas com conversas, tirando dúvida, pelos ensinamentos, pela paciência e amizade. Muito obrigada.

Agradeço a todas as pessoas que colaboraram com esse trabalho, sem as quais eu não poderia me dedicar a um estudo tão amplo de um mesmo material. Estas pessoas são: o Prof. Dr. Raimundo Lora Serrano da Universidade Federal de Uberlândia, e seus alunos Robert Prudêncio Amaral e Jeann César Rodrigues de Araújo, responsáveis pelo crescimento da amostra deste material; o Prof. Dr. Rafael Sá de Freitas do IFUSP pelas medidas físicas em baixas temperaturas da amostra; o Prof. Dr. Eric de Castro e Andrade da física da USP de São Carlos pela colaboração com referências e sua experiência no que se refere à teoria.

Estendo meus agradecimentos ao Laboratório Nacional de Luz Síncrotron (LNLS/CNPEM) em Campinas, seus funcionários e pesquisadores, pelo aprendizado, tempo cedido de beamline pra este estudo e outros experimentos. Ao *Laboratory for Muon Spin Spectroscopy* do Paul Scherrer Institute (PSI) na Suíça pelo tempo cedido ao meu orientador para medida de μ SR, aos seus pesquisadores pela ajuda e contribuição. Ao *Institute for Solid State and Material Physics* em Dresden, na Alemanha, pelos colaboradores na análise desses dados.

Ainda agradeço à Universidade de Uppsala na Suécia e ao programa Erasmus+, pela bolsa e oportunidade de ampliar minhas experiências e aprendizado durante o mestrado através do intercâmbio. Aos que foram receptivos e amigáveis, meus agradecimentos.

Agradeço aos meus pais: Maria Luiza e Joaquim, pelo apoio incondicional, o amor e me proporcionarem a oportunidade de estudar, ainda que eles mesmos não a tiveram. À minha melhor amiga desde a concepção e gêmea: Marisa, pelo exemplo e presença constante. Minhas irmãs: Miriam e Marlete. À minha família de sangue e coração: Josi, Silvio, Ana, Rafael e Luisa. Aos amigos: Luiz, Alexandre, Letícia, Luane, Henrique, Andrei, Otávio e Bartira pelos desabafos e momentos de diversão, jogos de tabuleiro e card games, videogame, álcool e karaokê. Muito obrigada.

Aos funcionários do IFUSP: segurança, limpeza, cpg, aos professores que me apoiaram, ensinaram e incentivaram, aos amigos do instituto e colegas pelas conversas e companhia.

Agradeço à Olimpíada Brasileira de Matemática das Escolas Públicas (OBMEP), aos seus idealizadores, autoridades que apoiaram o projeto e aos professores mais apaixonados e dedicados que eu conheci devido à esta competição. Agradeço ao incentivo para melhorar a qualidade

de ensino de exatas nas escolas públicas e trazer alunos da classe baixa para exatas nas universidades públicas.

Obrigada aos membros da banca pela leitura e considerações sobre este trabalho e ao CNPq, sem o qual, através da bolsa auxílio, eu seria impossibilitada de me dedicar à pesquisa.

Abstract

This work presents macroscopic and microscopic experiments of the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, in order to characterize its electronic, magnetic and structural properties to support the possibility that this system hosts a spin liquid phase. Such assumption is based on the absence of a transition to a magnetically ordered phase in the magnetic and thermodynamic measurements, which points to a strong magnetic frustration in this material. In addition, it is observed the formation of a correlated spin state. To characterize this correlation, we resorted to Muon Spin Resonance (μSR) experiments to measure the low temperature spin dynamics. The zero field μSR relaxation regime displays dynamic magnetism down to $T = 0.019$ K and longitudinal field experiments support as well that dynamic magnetism persists at low temperatures, a behavior expected for a spin liquid system. The magnetic behavior of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ consists in the high temperature physics being dominated by the presence of magnetic trimers, magnetic dimers, and orphan spins. At lower temperatures, the effective magnetic degrees of freedom, composed by orphan spins and magnetic trimers, are correlated but no phase transition is detected down to $T = 0.1$ K, despite the effective exchange couplings between magnetic trimers and orphan spins being ≈ -8.5 K, resulting in a magnetic frustration parameter of at least 85. The possibility that disorder is responsible for the spin liquid ground state is discussed, however, other scenarios are not totally discarded. For example, the possibility that the measured state is not the true ground state, which could lie at even lowers temperatures or the possible formation of a spin glass state. This work raises questions that are not easy to answer. Ultimately, the growth of a single crystal is necessary to continue the characterization of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. Besides, theoretical and experimental developments in this field of research are needed to find a more direct and conclusive way to characterize the magnetic phases in this complex material.

Keywords: quantum spin liquid; magnetic frustration; experimental characterization.

Resumo

Neste trabalho apresento dados experimentais macroscópicos e microscópicos da perovskita hexagonal dupla $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, a fim de caracterizar suas estruturas eletrônica, magnética e cristalina para embasar a possibilidade deste sistema apresentar uma fase de líquido de spin. Esta hipótese está baseada na ausência de transição para uma fase magneticamente ordenada nas medidas magnéticas e termodinâmicas, que apontam para uma forte frustração magnética neste material. Além disso, é observada a formação de um estado de spins correlacionados. Para caracterizar esta correlação, recorreremos para experimentos de ressonância de múons (μSR) para medir a dinâmica de spins em baixas temperaturas. Dados de μSR para campo magnético nulo mostram em seu regime de relaxamento um magnetismo dinâmico para temperaturas tão baixas quanto $T = 0.019$ K. Adicionalmente, experimentos com campo magnético longitudinal aplicado apontam também que o magnetismo dinâmico persiste em baixas temperaturas, um comportamento esperado para um sistema de líquido de spin. O comportamento magnético do $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ consiste na física de altas temperaturas sendo dominada pela presença de trimers magnéticos, dimers magnéticos e spins órfãos. Para temperaturas mais baixas, os graus de liberdade magnéticos são efetivamente compostos por spins órfãos e trimers magnéticos, que estão correlacionados mas nenhuma transição de fase é detectada para temperaturas tão baixas quanto $T = 0.1$ K, mesmo que a constante de interação efetiva entre os spins órfãos e os trimers magnéticos seja ≈ -8.5 K, resultando num fator de frustração magnética de ao menos 85. A possibilidade da desordem ser responsável pelo estado fundamental de líquido de spin é discutida, no entanto, outros cenários não estão totalmente descartados, por exemplo, a possibilidade de que o estado medido não seja o verdadeiro estado fundamental, e que este estaria em temperaturas ainda mais baixas ou a possível formação de um estado de vidro de spin. Este trabalho levanta questões que não são fáceis de responder. Por fim, o crescimento de uma amostra monocristalina é necessário para continuar a caracterização do $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. Ademais, desenvolvimentos de cunho teórico e experimental neste campo de pesquisa são necessários para encontrar um método mais direto e conclusivo para caracterizar a fase magnética neste material complexo.

Palavras-chave: spin líquido quântico; frustração magnética; caracterização experimental.

Contents

List of Figures

List of Tables

1	Introduction	13
2	Crystal and Electronic Structure	21
2.1	X-Ray Diffraction (XRD)	23
2.2	Resonant X-Ray Diffraction (RXD)	23
2.2.1	Theory of resonant scattering	23
2.2.2	Synchrotron X-Ray Diffraction Instrumentation	25
2.2.3	Resonant X-Ray Diffraction of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$	26
3	Thermodynamics and Magnetism	33
3.1	Theory of Exchange interaction	33
3.1.1	Superexchange interaction	34
3.2	Thermodynamic and magnetic data modeling	34
3.2.1	Ordered counting	35
3.2.2	Disordered counting	35
3.3	Magnetic Susceptibility	36
3.4	Magnetization	40
3.5	Specific Heat	41
3.5.1	Zero Field Magnetic Entropy	46
3.5.2	Schottky anomaly calculation	47
4	Microscopic Measurements	51
4.1	Muon Spin Resonance (μSR)	51
4.1.1	Muon production, implantation and detection	51
4.1.2	μSR data and analysis for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$	52
5	Discussion, Summary and Conclusion	59
5.1	Emerging Magnetic Sub-lattice	59
5.2	The Nature of the Dynamic Magnetic State	62
5.3	Summary and Conclusion	64
	Bibliography	67

CONTENTS

List of Figures

1.1	Representation of geometric frustration and by competition.	15
1.2	(a) Ground state of the triangular lattice with first neighbors interaction in the Heisenberg model; (b) Kagome lattice.	16
1.3	Kitaev lattice formed by two ions basis in a triangular lattice.	17
1.4	Structural model of the hexagonal double perovskite-type structure $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, showing Barium sites $Ba(1)$ and $Ba(2)$, Oxygen $O(1)$ and $O(2)$, Titanium $M(3)$ and Manganese $M(1)$, as well the mixed Ti and Mn site $M(2)$. In the right details of structural trimer, with exchange constants J_1 and J_2	18
1.5	The magnetic trimer, magnetic dimer and orphan spin in the structural trimer. The phenomenological constants related to each model are written in red. . . .	18
2.1	Representative scheme of a synchrotron light source. Image downloaded from https://www.diamond.ac.uk/Public/How-Diamond-Works.html in February 2019.	25
2.2	Schematic layout of the XRD1 beamline at LNLS-CNPEM. Image downloaded from https://www.lnls.cnpem.br/linhas-de-luz/xrd1/overview in February 2019.	26
2.3	Refinements of X-ray diffraction for different incident photon energy using model 1 for the atom occupancies. The Mn K-edge energy is 6539 eV. The red symbols and the black solid lines represent the observed and calculated patterns, respectively. The blue curve shown at the bottom is the difference. Pink vertical bars indicate the expected Bragg peak positions according to the structure model.	28
3.1	Magnetic susceptibility ($\chi(T)$) data as a function of T ($0.6 \leq T \leq 330$ K). The red line represents the data fitted to the model in equation 3.8. The insert shows $\chi(T)$ for $T < 12$ K.	36
3.2	AC Susceptibility ($\chi'(T)$) measurements as a function of T ($1.8 < T < 300$ K) at distinct frequencies.	40
3.3	Isothermal magnetization ($T = 0.6$ K) as a function of H ($M(H)$).	41
3.4	specific heat ($C_p(T)$) data as a function of T and applied magnetic field H . . .	42
3.5	$\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ specific heat data ($H=0$) compared with the BaTiO_3 specific heat.	42
3.6	Magnetic specific heat ($C_{\text{mag}}(T)$) after the lattice contribution of Figure 3.5 subtraction.	43
3.7	Nuclear specific heat of MnNi in contrast with the low temperature specific heat of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$	44
3.8	Magnetic specific heat fitting in the low T region ($0.3 < T < 1.0$ K) to the expression $C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)}$ for different values of H	45
3.9	$\alpha(H)$ and $\gamma(H)$ parameters from the fitting in Figure 3.8.	45

3.10	Magnetic specific heat for zero field and the corresponding magnetic entropy $\Delta S(T)$. For the region $0.01 < T < 0.3$ K the data is calculated from the fitting shown in Figure 3.8.	47
3.11	Calculated magnetic specific heat for the dimer system. The result is field independent and negligible in the low temperature limit.	48
3.12	Calculated magnetic specific heat for the trimer system. The result is field dependent and Schottky anomalies appear with the influence of an external magnetic field.	49
3.13	Comparison between the calculated trimer Schottky anomaly and experimental data for $H = 1$ T and $H = 9$ T.	50
4.1	μ SR spectra for zero field in the crossover region ($1.5 < T < 10$). The lines are fittings to the stretched exponential of equation 4.5. All data is from GPS spectrometer.	53
4.2	μ SR spectra for zero field in the lowest temperature region ($T < 1.5$ K). The line is the fitting of the $T = 0.019$ K data to the stretched exponential of equation 4.5, and is representative of all temperatures in the graph. All data is from LTF spectrometer.	54
4.3	Coefficients: relaxation rate λ and the exponent β as a function of temperature T for both GPS and LTF spectrometers.	54
4.4	Asymmetry profile of the longitudinal field (LF) data for $T = 0.1$ K and different magnetic fields. The lines are the expected spectra in the DKT theory.	56
4.5	The red circles are the relaxation rate λ for different values of magnetic field (H) for the LF data. The blue line refers to the fitting to the equation 4.9. . . .	57
5.1	Model of the proposed emerging magnetic lattice at low temperatures. The lattice parameter is $5.691 \text{ \AA}$. The trimer-orphan distance is $9.868 \text{ \AA}$, represented by the dashed yellow line. The full yellow line represents the displacement between the two planes. The oxygen atoms were omitted in the octahedra for the visualization.	60
5.2	Four layers stack of triangular lattices as a possible magnetic emerging lattice. The blue layers are composed by orphan spins only, with $S = 3/2$, and the red layers are composed by magnetic trimers, that in low temperature are effective $S = 1/2$	61
5.3	Model of the proposed disordered emerging magnetic lattice at low temperature. Half of the M(2) sites are filled with Mn atoms (purple) and the other half by Ti atoms (blue), in a disordered way, that is statistically determined.	62

List of Tables

2.1	Refined structural parameters from neutron powder diffraction for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ at room temperature.	22
2.2	Average bond length and lattice parameters given by Table 2.1 refinement. . . .	22
2.3	Different models used to refine the resonant X-ray diffraction data and its relative atom occupancy in the sites M(2) and M(3).	27
2.4	Refinement statistical factors for different energies and different models for the M(2) and M(3) site occupancy. The highlighted values are the smaller ones. . .	28
2.5	Refinement results for X-ray incident energy of 6500 eV and using the model 1 for the occupancy.	29
2.6	Refinement results for X-ray incident energy of 6535 eV and using the model 1 for the occupancy.	29
2.7	Refinement results for X-ray incident energy of 6564 eV and using the model 1 for the occupancy.	29
2.8	Refinement results for X-ray incident energy of 12000 eV and using the model 1 for the occupancy.	30
2.9	Refinement results for X-ray incident energy of 6500 eV and using the model 2 for the occupancy.	30
2.10	Refinement results for X-ray incident energy of 6535 eV and using the model 2 for the occupancy.	30
2.11	Refinement results for X-ray incident energy of 6564 eV and using the model 2 for the occupancy.	31
2.12	Refinement results for X-ray incident energy of 12000 eV and using the model 2 for the occupancy.	31
2.13	Refinement results for X-ray incident energy of 6500 eV and using the model 3 for the occupancy.	31
2.14	Refinement results for X-ray incident energy of 6535 eV and using the model 3 for the occupancy.	32
2.15	Refinement results for X-ray incident energy of 6564 eV and using the model 3 for the occupancy.	32
2.16	Refinement results for X-ray incident energy of 12000 eV and using the model 3 for the occupancy.	32
3.1	Fitting values from the magnetic susceptibility model, using the two different counting for the fraction of trimers, dimers and orphan spins.	39

LIST OF TABLES

Chapter 1

Introduction

Magnetism is one of the most intriguing and interesting phenomena in Physics. It has been observed since ancient times, but its scientific theory dates back from a couple of centuries ago and it was better understood only more recently, with the development of quantum mechanics. Based on quantum mechanics, we learned that the basic unit of the magnetism is the spin of a particle, which is an intrinsic property, like its mass or charge. In condensed matter Physics, it is usually the electron spin that we are interested in.

In magnetic systems, a ground state with long range order may arise from the interaction between the spins. Long range order relates to a phase transition, which can be interpreted as a spontaneous symmetry breaking in the Landau theory. We are able to understand phenomena such as ferromagnetism and antiferromagnetism in this framework. It can be applied as well to more complex phenomena, such as superconductivity.

In this work the intention is to characterize the low temperature magnetic behavior in the material $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, with a disordered hexagonal double perovskite type structure. There is the possibility that the ground state is a spin liquid, which cannot be understood in the framework of the Landau theory. In the following chapters will be discussed experiments concerning the structural, electronic, thermodynamic and magnetic properties of this system. In this chapter, an introductory explanation about a spin liquid state and its observation is provided.

The meaning of the term Spin Liquid has changed over the years [1]. The term was first introduced by P. W. Anderson in 1973 [2] and it can generally be understood as an exotic magnetic ground state, wherein a system of interacting localized spins, even at a temperature much lower than the energy scale of the interactions, do not display magnetic order. Therefore, dynamic behavior of the spin system is preserved even in the presence of strong interactions, characterizing a cooperative paramagnetic state [3].

Current understanding points that the magnetic frustration is the mechanism behind the formation of a spin liquid state. Magnetic frustration occurs when the interaction of localized spins in a lattice have contradictory constraints, due to competition, dimensionality, geometry or anisotropy [4]. As a consequence, the symmetry breaking is delayed to lower temperatures, with the possibility of being totally suppressed down to the zero temperature limit. In this case,

it gives origin to an exotic state such as the spin liquid, in which fractionalized excitations may appear [5]. Fractionalization means that the excitations in the system present quantum numbers that are not multiples of its constituents. In the case of magnetic excitations, it is constituted by electron spins, with $S = 1/2$.

Other exotic magnetic ground states formed by the presence of magnetic frustration are spin glass and spin ice. A spin ice is a state in analogy to the water ice: the spins are frozen under a given temperature, presenting a macroscopic residual entropy per spin originated from the degeneracy of the ground state [6]. The magnetic order in spin ices is analogue to the positional order of atoms in the water ice. The canonical spin ice occurs experimentally for ferromagnetic interactions in a pyrochlore lattice, which is a lattice of corner-sharing tetrahedra [7], and as we shall see, it does not fit in the experimental features of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$.

The spin glass is, in turn, in an analogy with the typical glass: the spins are frozen, under a given temperature, in a state where the spins are randomly oriented, presenting disorder, but has a locally correlated phase. The ground state of such system is hard to determine, with the formation of many different metastable states, which is similar to a conventional glass. It can occur by the dilution of a spin ice system, as well as a result of disorder.

The differences between the definitions of spin ice and spin glass are subtle, but just as water ice and conventional glass, the experimental behavior is altogether different. Experimentally, the spin glass is much closer to a spin liquid, the main difference lying in the level of quantum fluctuations: it is much bigger in a spin liquid state than in a spin glass.

All these exotic magnetic ground states deviate from the Curie behavior of mean field theory. To model the deviation in paramagnetic response in the high temperature limit, we resort to the Curie-Weiss model for magnetic susceptibility:

$$\chi = \frac{C}{T - \Theta_{\text{CW}}}, \quad (1.1)$$

where C is the Curie constant and Θ_{CW} is the Curie-Weiss temperature, given as:

$$C = n g^2 \mu_B^2 \frac{S(S+1)}{3k_B} \quad (1.2)$$

$$\Theta_{\text{CW}} = zJS(S+1)/3k_B, \quad (1.3)$$

with z as the coordination number relative to the first neighbors, $n = N/V$ represents the population of spins, J is the exchange constant describing the interaction among the spins, g is the gyromagnetic ratio and S is the spin quantum number of the specific magnetic ion, resulting from the electrons in its electronic shell. k_B is the Boltzmann constant and μ_B is the Bohr magneton.

In a mean field approximation, a phase transition is expected to an ordered state at about Θ_{CW} . It is then suggested to define a magnetic frustration parameter f (or frustration factor),

comparing the expected transition temperature to the observed one. Therefore, f can be defined as in equation 1.4 [8, 9], with T_c being the critical temperature where a phase transition occurs. This parameter indicates how much the system deviates from mean field theory, for which $f = 1$.

$$f \equiv \frac{|\Theta_{\text{CW}}|}{T_c} \quad (1.4)$$

The frustration parameter measures the magnitude of the system magnetic frustration. In frustrated systems the paramagnetic phase extends for $T \ll \Theta_{\text{CW}}$, resulting in a large f . If no transition is observed at all, instead of T_c the smallest measured temperature for which the system do not show long range order is adopted. Thus, a perfect spin liquid would have $f \rightarrow \infty$.

The most classic example of magnetic frustration is the triangular lattice with antiferromagnetic (AFM) interactions. This is illustrated in Figure 1.1. This frustration has a geometric origin, since the lattice can not intrinsically satisfy all first neighbors interactions simultaneously.

It is easier to picture the magnetic frustration on two-dimensional lattices, but it also occurs on three-dimensional lattices, such as tetrahedral lattice with AFM interactions, also shown in Figure 1.1. This tetrahedral frustration is the base for the magnetic frustration in pyrochlore oxides, a family of materials well known for presenting spin ice, spin glass and spin liquid behavior [10].

Figure 1.1: Representation of geometric frustration and by competition.

The square lattice is not geometrically frustrated in its first neighbors interactions. However, with AFM interaction between second neighbors, the lattice will become frustrated. This kind of frustration is termed frustration by competing interactions.

Back to the triangular lattice, if the interactions are anisotropic, the ground state is degenerated and it does not show long range order even in the zero temperature limit, which is the most simple example of a spin liquid concept. It was experimentally shown in Cs_2CuCl_4 , where the triangular lattice interactions are anisotropic [11].

The realization of triangular lattice spin liquids also occurs in YbMgGaO_4 [12], which has disorder in the Mg/Ga non-magnetic sites. Another family of triangular lattice spin liquid candidates materials are the rare-earth chalcogenides AReCh_2 (A = alkali or monovalent ions, Re = rare earth, Ch = O, S, Se) [13], where there is no disorder in the structure.

However, if the triangular lattice has isotropic interactions, like Heisenberg interaction, the spin system will eventually reach long range order with a ground state where each spin is aligned 120° with its first neighbors [14], as shown in Figure 1.2a. Thus, this does not result in a spin liquid state.

An example of a lattice which is magnetically frustrated and has a degenerated ground state even with Heisenberg interactions, is the Kagome lattice. It is defined by a triangular lattice with three atoms in the basis, as shown in Figure 1.2b. In a Kagome lattice with Heisenberg interactions the ground state will be a spin liquid [15].

Figure 1.2: (a) Ground state of the triangular lattice with first neighbors interaction in the Heisenberg model; (b) Kagome lattice.

The frustration in the Kagome lattice was systematically studied in the jarosite family of materials [16], and the spin liquid behavior was characterized in the materials $\text{ZnCu}_3(\text{OH})_2$ [17], $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (known as volborthite) [18, 19] and in the paratacamite family [20].

To achieve a triangular or a Kagome lattice in a three-dimensional material, usually the system is separated in two-dimensional layers of interacting spins. The layers are magnetically isolated from each other by a large distance and/or by intercalating the magnetic layers with non magnetic ions. This way, most spin liquid candidate materials have a two-dimensional magnetic lattice.

Spin liquid candidate materials are also observed for which the magnetic lattice is two-dimensional but it organizes in magnetic bilayers, which are, however, isolated from each other. One example is the Kagome bilayer of Cr^{5+} ions in $\text{Ca}_{10}\text{Cr}_7\text{O}_{28}$ [21].

Another two-dimensional lattice that frequently appears for modeling magnetic frustration and spin liquid candidates is the Kitaev lattice, also known as honeycomb lattice, that is illustrated in Figure 1.3. If we compare the triangular, the Kitaev and the Kagome lattices, it is possible to see that these lattices are all based on the triangular geometry, differing only on the number of atoms on the basis. As a consequence, they differ as well on the number of first neighbors (and consequentially on the number of interactions to obey), that are six, three and four respectively.

Figure 1.3: Kitaev lattice formed by two ions basis in a triangular lattice.

The Kitaev model was theoretically studied by Kitaev [22], where he modelled the mathematical phases in the space parameter for a $S = 1/2$ honeycomb lattice with anisotropic interactions. Experimental realization of this lattice was made in the Iridium Oxides $A_2\text{IrO}_3$ ($A = \text{Na}, \text{Li}$), also known as Iridates, where a spin liquid phase was predicted in a certain region of parameter space [23]. However, these compounds were characterized to have a magnetically ordered Mott insulator phase, undergoing antiferromagnetic phase transition for $T_N \approx 15$ K. The Li_2IrO_3 material, however, is close to the spin liquid phase [24, 25].

The characterization of a spin liquid phase for the Kitaev model was also attempted in αRuCl_3 [26, 27], and this material seems to be close to the spin liquid behavior since evidence of fractionalized excitations have been found in spectroscopic measurements [28, 29]. However, it still shows antiferromagnetic order. Developments have been made based on these materials to achieve the experimental realizations of the Kitaev model.

Spin liquid studies are part of the challenge of understanding spin physics beyond the Landau theory and, as was shown, it has been extensively studied in the past years and there are several experimental attempts of reproductions and characterization of this solid state phase. The characterization process is based on structural properties, as well as electronic, thermodynamic and magnetic properties. Macroscopic and microscopic data are analyzed together to model a scenario that is complete and cohesive.

The goal in this area of Physics for the next years consists on developing a proper experimental characterization method of a spin liquid phase that is unambiguous, which may rely on the respective theoretical development.

In this work the subject of study is the system $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, with a hexagonal double perovskite-type structure, first proposed by G. M. Keith in 2004 [30] and shown in Figure 1.4. The magnetic ion in the system is Mn^{4+} with $S = 3/2$, coordinated by an oxygen octahedron. The oxygen atoms are the mediators of a superexchange antiferromagnetic interaction between the Mn atoms [31], which are placed in structural trimers formed by face sharing octahedra. These structural trimers have three possible occupations: three Mn, defining a magnetic trimer; two Mn and one Ti, defining a magnetic dimer or one Mn and two Ti, defining an orphan spin,

Figure 1.4: Structural model of the hexagonal double perovskite-type structure $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, showing Barium sites $Ba(1)$ and $Ba(2)$, Oxygen $O(1)$ and $O(2)$, Titanium $M(3)$ and Manganese $M(1)$, as well the mixed Ti and Mn site $M(2)$. In the right details of structural trimer, with exchange constants J_1 and J_2 .

as illustrated in Figure 1.5.

Figure 1.5: The magnetic trimer, magnetic dimer and orphan spin in the structural trimer. The phenomenological constants related to each model are written in red.

In a 2015 paper [32], X-ray Absorption Spectroscopy (XAS) data was presented, in addition to neutron diffraction, magnetic susceptibility and Electron Spin Resonance (ESR) of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. In that occasion it was hypothesized that a spin liquid phase may occur in this material.

In this work, the goal is to complement the material characterization, having in mind the experimental features of a spin liquid. For this, we present experimental data of specific heat, magnetic susceptibility, magnetization, resonant X-ray Diffraction (XRD) and Muon Spin Resonance (μSR). It is also presented some theoretical analysis and simulations which are very

important to the understanding and correct interpretation of the experimental data.

The intention is to explain the magnetic frustration mechanism, referring to the recent theoretical modelling and experimental examples.

In chapter 2 the crystalline and electronic structures are presented, in which synchrotron methods were used. The thermodynamic and magnetic aspects are explained in chapter 3, while the spin dynamics and the microscopic characterization are presented in chapter 4. In chapter 5 there is an discussion that takes into account all previous data and theoretical considerations about the magnetic ground state of the system.

Chapter 2

Crystal and Electronic Structure

Usually, the theory used to model magnetism in solid state physics is divided in two opposite limits: *localized magnetism* and *itinerant magnetism*. These limits are representative of real materials however, it is not unusual that a given material will present both aspects experimentally.

Keeping this in mind, $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ is an oxide and does not exhibit a metallic behavior, which means its magnetism can be thought as localized. Local moment magnetism raises the importance of the crystallographic lattice in the description of magnetic properties.

The structure of the oxide $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ is presented in Figure 1.4. It is a hexagonal double perovskite-type structure, with space group $R\bar{3}m$, first proposed by Keith et al. [30]. Magnetic and electronic properties were later and characterized [32] using neutron diffraction. Its electronic structure was investigated using X-ray Absorption Spectroscopy (XAS) of the Mn K edge [32]. The neutron diffraction data is summarized in Table 2.1 and 2.2. Because of the similarity of the scattering lengths for Mn and Ti, the relative occupation of the transition metal sites could not be distinguished. As we shall discuss below, this was determined in the literature based on certain assumptions concerning the chemical properties of the cations. In this work, we present Resonant X-Ray Diffraction at the Mn K edge to support the modelled site occupancy for the transition metal sites.

Information about the local electronic structure of the Mn cations can be inferred by observing the near edge structure of the absorption spectra, which is called the XANES (X-ray Absorption Near Edge Spectroscopy) region. XANES of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ at the Mn K edge shows that the Mn cations in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ have the same structure of the Mn K-edge XANES spectra of BaMnO_3 , which means that the Mn cations in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ are in a +4 valence state. Based on this result, we can conclude that the only ions carrying a net magnetic moment are the Mn^{4+} cations. In this oxidation state, the Mn electronic structure is $3d^3$ corresponding to $S = 3/2$.

The transition metal sites M(1), M(2) and M(3) in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ structure are coordinated by oxygen octahedra. The sites M(1) and M(2) form a structural trimer of face-sharing octahedra. The distinct trimers are connected by corner-sharing octahedra, inside which lies the

M(3) sites.

Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.2856 (2)	0.76 (9)
Ba(2)	6c	1.0	0	0	0.1290 (2)	0.12 (6)
M(1) Mn	3b	1.0	0	0	0.5	0.0 (1)
M(2) Mn/Ti	6c	0.5/0.5	0	0	0.4091 (2)	0.2 (1)
M(3) Ti	3a	1.0	0	0	0	0.1 (1)
O(1)	18f	1.0	0.1513 (2)	0.8487 (2)	0.45656 (8)	0.42 (4)
O(2)	18f	1.0	0.1673 (3)	0.8327 (3)	0.62700 (9)	0.63 (4)

Table 2.1: Refined structural parameters from neutron powder diffraction for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ at room temperature.

Since the X-ray scattering length for Mn and Ti are very similar, the occupation could not be resolved by X-ray diffraction. Therefore, it was suggested that the transition metal sites could have a mixed occupancy [30, 33], including the non magnetic Ti^{4+} ion and the $S = 3/2$ Mn^{4+} ion. The original occupation model was then based in the average bond length between the transition metal and the oxygen in the coordination structure. In this scheme, the occupancies are as shown in Table 2.1.

The M(1) site is exclusively filled with Mn, since its average bond length is compatible with usual chemical bond between Mn and O. Analogously, the M(3) site is exclusively filled by Ti, due to the average bond length between the transition metal and the oxygen being close to usual Ti-O bond length. Therefore, by the stoichiometry of the compound, it is expected that the M(2) site would be half filled by Mn and half filled by Ti. This assumption can be reinforced by the average bond length being a intermediary one, considering the M(2)-O(1) and M(2)-O(2) bonds.

Average Bond Length		Lattice parameters	
M(1)-O(1)	1.922 (2) $\text{\AA}$	a	5.6910 (3) $\text{\AA}$
M(2)-O(1)	1.995 (5) $\text{\AA}$	b	5.6910 (3) $\text{\AA}$
M(2)-O(2)	1.932 (4) $\text{\AA}$	c	27.915 (1) $\text{\AA}$
M(3)-O(2)	1.976 (3) $\text{\AA}$	Space group $R\bar{3}m$	

Table 2.2: Average bond length and lattice parameters given by Table 2.1 refinement.

The magnetic sub-lattice formed in the system, from which it is expected to explain its frustration, depends on the transition metal sites occupancies. As explained above, the Mn cations in this system have a non zero spin, while the spin of Ti cations are zero. Thus, the structural trimers formed by the transition metal sites M(1) and M(2) have different magnetic effects in the lattice depending on the M(2) site occupancy, which is shown in Figure 1.5 and better studied in the chapter 3. That is the reason why the occupancy of this site is so important for the magnetic characterization of the $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, and why we had taken resonant X-ray

diffraction data in the energy of the Mn K edge to resolve the transition metal sites occupancy, which is explained in the section 2.2.

2.1 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a widespread used and powerful technique, in which a incident X-ray beam is scattered by atoms arranged in a periodic array over the sample. It gives origin to a interference patter that is constructive in some angles, determined by the Bragg's Law, shown in equation 2.1.

$$\lambda = 2d_{hkl}\sin\theta \quad (2.1)$$

In the experiments, the wavelength λ (or energy) is fixed, and the incident angle moves over the sample, giving origin to peaks at certain angles θ , in a typical diffraction pattern. The distance between parallel planes of atoms in the sample is d_{hkl} , where (hkl) is a family of planes. The length of λ is close to the distance between atoms in lattice, being an appropriate probe to measure the lattice distances.

However, usually the XRD pattern is measured using a polycrystalline sample, that means, a powder sample, in with several tiny crystals are at random directions. Thus, the diffraction pattern is averaged over all directions of the crystal.

The position (angle) of the peaks at the diffraction follows from the Bragg's law. But the intensity of these peaks is derived from the structure factor, which depends on the atomic position and each atom form factor. This factor is proportional to the atomic number Z , thus it is very similar to Mn ($Z = 25$) and Ti ($Z = 22$). This justify the use of Resonant X-Ray Diffraction, as explained in the following section.

2.2 Resonant X-Ray Diffraction (RXD)

2.2.1 Theory of resonant scattering

The Resonant X-ray Diffraction (RXD), also called anomalous diffraction, is the result of the relation between absorption process and X-ray diffraction (XRD), by changing the incident X-ray energy to one of the absorption edges of one element in the material.

Based on the current synchrotron light sources availability worldwide, which allows a great range of continuous X-ray energy, it is very common to use absorption energies in several measurements types and geometries. These energies give access to an amount of information that is not available in the fixed energies of the common X-ray source. An example is the effect that the absorption has in the X-ray diffraction relative intensities.

In this way, it is possible to use Resonant X-ray diffraction to resolve the site occupancy between two atoms with very similar scattering length (in a energy out of resonance) in a complex structure, which is precisely our case.

Theoretical considerations for the diffraction and absorption processes are based on the matter-radiation interaction Hamiltonian. The absorption process in this case is considered to be elastic: a core electron is excited to a higher level, which is not stable. Then, it decays to its original energy, emitting a photon of same energy as the incident X-ray.

It is possible to separate the most relevant terms and processes for the X-ray scattering and model the intensity for the detected X-ray, as shown in equation 2.2 [34].

$$I(\omega, \mathbf{Q}) \propto \left| \sum_j e^{i\mathbf{Q} \cdot \mathbf{R}} (f_j(\mathbf{Q}) + f'_j(\omega) + if''_j(\omega)) \right|^2 \quad (2.2)$$

Where $\mathbf{Q}$ and $\mathbf{R}$ are the lattice dependant factors of momentum transfer and atoms crystallography position respectively, and the f factors are scattering length factors which are element sensitive and are given in units of number of electrons per atom. $f_j(\mathbf{Q})$ is the atomic form factor referent to Thomson scattering, $f'_j(\omega)$ is the absorption real scattering factor and $f''_j(\omega)$ is the imaginary one. The term $f'_j(\omega) + if''_j(\omega)$ is called resonant scattering factor [35].

The f_j are real numbers, obtained by a Fourier transform of the charge distribution, and it is frequency (energy) independent. It increases with the atomic number Z , being very similar in the case of elements with similar Z . The $\mathbf{Q}$ dependency comes from the fact that all electrons participate in this scattering process.

On the other hand, the resonant scattering factor can be approximated to be momentum independent, because it refers to very localized K shell electrons, and sometimes L and M in the case of heavier atoms. It changes significantly in the energy range of the scatterer absorption edge, which makes it possible to use this energy to probe the crystal structure of materials with similar elements in its composition.

There are several approaches to estimate an expression to the resonant scattering factor, including semiclassical (to treat the electrons as forced harmonic oscillators) or numerical approaches [34]. The obtained expressions always have a resonant aspect to a given frequency. Another approach is to explain it using quantum mechanical theory: the core electron excitation and Thompson scattering can be explained by first-order perturbation theory in the matter-radiation interaction Hamiltonian. The decaying and photon emission would be a second-order process and the resonance would arise from the second-order perturbation theory expression [36], as shown in equation 2.3.

$$f'_j(\omega) + if''_j(\omega) = \sum_{n,g} \frac{\langle \phi_g^{(j)} | \hat{H}_R^* | \phi_n \rangle \langle \phi_n | \hat{H}_R | \phi_g^{(j)} \rangle}{\hbar\omega - (E_n - E_g) + i\frac{\Gamma}{2}}, \quad (2.3)$$

with $\phi_g^{(j)}$ as the core-state centered at site j and ϕ_n as all possible intermediate states with en-

ergy E_n and a lifetime of about $\hbar/\Gamma$. $\hat{H}_R$ is the term in the matter-light interaction Hamiltonian which is linear in the magnetic vector potential $\mathbf{A}(\mathbf{r}_i)$ and depends on the spin interaction as well, as defined in equation 2.4. The quadratic term in the magnetic vector potential is responsible for the Thomson scattering, and thus will explain the scattering process in the first-order perturbation theory.

$$\hat{H}_R = - \sum_i \frac{e}{m} [\mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i + \mathbf{s}_i \cdot (\nabla \times \mathbf{A}(\mathbf{r}_i))] \quad (2.4)$$

The quantum mechanical approach is the only one where it is possible to calculate by first principles in a quantitative way the absorption process. The semiclassical approach can shed some light in the phenomena, but not predict the absorption terms in the diffraction.

2.2.2 Synchrotron X-Ray Diffraction Instrumentation

Synchrotron is a type of circular particle accelerator. It can accelerate charged particles by the use of bending magnets. These magnets generate a field which bends the particle trajectory. Synchrotron rings are used to generate electromagnetic radiation from accelerated electrons, giving origin to a synchrotron light source.

To generate the light, the synchrotron light source includes the storage ring, responsible for maintain the velocity of the accelerated electron, the linear accelerator (linac), which injects the electron beam in the ring and usually a booster ring that accelerate the electrons before they are injected in the storage ring. This is illustrated in Figure 2.1.

Figure 2.1: Representative scheme of a synchrotron light source. Image downloaded from <https://www.diamond.ac.uk/Public/How-Diamond-Works.html> in February 2019.

The radiation emitted is always perpendicular to the electron trajectory, and consequently perpendicular to the storage ring. It is distributed to different beamlines, that are actually straight lines coming out of the storage ring, as shown in Figure 2.1. The instrumentation in the beamline changes accordingly to the used technique. A scheme of the beamline XRD1 at LNLS-CNPEM is shown in Figure 2.2, and is representative of most X-Ray Diffraction beamlines.

Figure 2.2: Schematic layout of the XRD1 beamline at LNLS-CNPEM. Image downloaded from <https://www.lnls.cnpe.br/linhas-de-luz/xrd1/overview> in February 2019.

The XRD1 beamline has a first slit followed by a focusing mirror, responsible for decrease the size of the X-ray beam, while it maintain its flux. Thereafter, the double-crystal monochromator (DCM) made by Si crystal selects only one frequency. Finally, two slits have the function of limiting the dimensions and divergence of the incident X-ray beam: the first does it vertically and the second horizontally. All this instrumentation precede the instrumental station. The detection is made by an one-dimensional X-ray detector, that work by photon counting.

2.2.3 Resonant X-Ray Diffraction of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$

Resonant XRD was performed using a polycrystalline sample of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. This sample were synthesized by Prof. Dr. Raimundo Lora Serrano group at *Universidade Federal de Uberlândia* using the solid-state reaction method, a commonly used method to synthesize samples of polycrystalline solids from a mixture of compounds that are solid at room temperature. Such compounds in this case are BaCO_3 , MnO_2 , and TiO_2 , which were mixed in a certain proportion, grounded and heated in air at 900°C for 24 hours in a tubular furnace. Later it was grounded and heated again, this time at 1100°C for 24 hours as well. Between these process, the material was checked by X-ray diffraction in order to verify its purity, meaning that it does not form a phase of a different material within the crystals. Thus, it was possible to obtain a highly pure sample of polycrystalline $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. Samples from the same batch were

used in all characterization methods presented also in the following chapters. The Synchrotron X-Ray diffraction experiments were performed at the Brazilian XRD1 beamline of the LNLS-CNPEM [37], with energy range between 5500 and 14000 keV. The experiment was performed for incident photon energies of 6500 eV, 6535 eV, 6564 eV and 12000 eV. The selected energies correspond, respectively, to below, slightly below, slightly above and greatly above the Mn absorption K-edge of 6539 eV.

The refinement was made using FullProf software package [38], for different models for the M(2) and M(3) site occupancy. Since the structure is very complex and the signal to noise ratio at the resonance energy region was not very good, it was not possible to refine the occupancies in the structure. Therefore, models with fixed occupancies are necessary to test the best scenario, and are outlined in Table 2.3.

Model1			Model2			Model3		
Site	Mn	Ti	Site	Mn	Ti	Site	Mn	Ti
M(1)	100%	0%	M(1)	100%	0%	M(1)	100%	0%
M(2)	50%	50%	M(2)	45%	55%	M(2)	40%	60%
M(3)	0%	100%	M(3)	10%	90%	M(3)	20%	80%

Table 2.3: Different models used to refine the resonant X-ray diffraction data and its relative atom occupancy in the sites M(2) and M(3).

It is supposed that the M(1) site is always fully filled by Mn. This is based on the fact that the average bond length between M(1) and O(1) corresponds closely to the value expected for Mn - O bonds [30, 32]. Moreover, from a magnetic point of view, for the superexchange to happen in the structural trimer, one magnetic ion is required at the central octahedron.

In Figure 2.3 it is possible to observe the refinement using model 1. Some peaks in the low angle region are not represented by the refinement because they correspond to residual peaks from the background subtraction. These peaks were originated from a starch substance used to dilute the sample in order to avoid detector saturation.

The algorithm used by the FullProf software minimizes the χ^2 instead of the Rietveld parameters, therefore it was our statistical factor to judge the quality of the refinements. Also, it should be noted that in the resonance region, the Debye-Waller coefficient and the oxygen positions were not refined due to the quality of the data.

In Table 2.4 it is possible to compare the statistical factors in the refinements for different values of energy and testing models for the transition metal sites occupancies. It should be noted that the models with small changes in the proposed occupancies (models 2 and 3) have similar statistics. However, model 1, or the proposed model in the literature, is systematically better in the resonant energy region.

The refinement results for all models and energies are also presented in Table 2.5-2.16.

Figure 2.3: Refinements of X-ray diffraction for different incident photon energy using model 1 for the atom occupancies. The Mn K-edge energy is 6539 eV. The red symbols and the black solid lines represent the observed and calculated patterns, respectively. The blue curve shown at the bottom is the difference. Pink vertical bars indicate the expected Bragg peak positions according to the structure model.

Energy (eV)	Occupancy	BRAGG R-Factors		Rietveld R-factors		χ^2
		Bragg R	RF	R _{wp}	R _{exp}	
12000	Model1	21.3	21.6	17.8	7.89	5.18
	Model2	18.2	20.8	17.8	7.90	5.19
	Model3	19.3	20.9	17.8	7.90	5.16
6500	Model1	18.2	14.9	33.8	15.84	4.55
	Model2	18.3	14.9	33.8	15.84	4.55
	Model3	18.3	15.1	33.8	15.84	4.55
6535	Model1	19.3	15.5	32.8	15.43	4.51
	Model2	19.4	15.6	32.8	15.43	4.53
	Model3	19.4	15.6	32.8	15.43	4.53
6564	Model1	24.6	20.2	38.6	22.43	2.97
	Model2	24.7	20.5	38.7	22.43	2.98
	Model3	24.6	20.5	38.7	22.43	2.98

Table 2.4: Refinement statistical factors for different energies and different models for the M(2) and M(3) site occupancy. The highlighted values are the smaller ones.

M1: 6500 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.5/0.5	0	0	0.403 (2)	0.05
M(3) Ti	3a	1.0	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05
a = b = 5.690 (5) $\text{\AA}$, c = 27.90 (4) $\text{\AA}$, $R_{\text{wp}} = 33.8\%$, $R_{\text{exp}} = 15.84\%$, $\chi^2 = 4.55$						

Table 2.5: Refinement results for X-ray incident energy of 6500 eV and using the model 1 for the occupancy.

M1: 6535 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.5/0.5	0	0	0.402 (2)	0.05
M(3) Ti	3a	1.0	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05
a = b = 5.688 (5) $\text{\AA}$, c = 27.89 (4) $\text{\AA}$, $R_{\text{wp}} = 32.8\%$, $R_{\text{exp}} = 15.43\%$, $\chi^2 = 4.51$						

Table 2.6: Refinement results for X-ray incident energy of 6535 eV and using the model 1 for the occupancy.

M1: 6564 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.5/0.5	0	0	0.402 (3)	0.05
M(3) Ti	3a	1.0	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05
"a = b = 5.687 (6) $\text{\AA}$, c = 27.89 (4) $\text{\AA}$, $R_{\text{wp}} = 38.6\%$, $R_{\text{exp}} = 22.43\%$, $\chi^2 = 2.97$ "						

Table 2.7: Refinement results for X-ray incident energy of 6564 eV and using the model 1 for the occupancy.

M1: 12000 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.2856 (3)	0.54 (2)
Ba(2)	6c	1.0	0	0	0.1286 (3)	0.21 (2)
M(1) Mn	3b	1.0	0	0	0.5	0.16 (4)
M(2) Mn/Ti	6c	0.5/0.5	0	0	0.4071 (8)	0.35 (4)
M(3) Ti	3a	1.0	0	0	0	0.42 (4)
O(1)	18f	1.0	0.148 (4)	0.852 (4)	0.457 (2)	0.11 (7)
O(2)	18f	1.0	0.154 (6)	0.846 (6)	0.629 (2)	0.17 (9)

"a = b = 5.6934 (3) $\text{\AA}$, c = 27.922 (2) $\text{\AA}$, R_{wp} = 17.8%, R_{exp} = 7.89%, χ^2 = 5.18"

Table 2.8: Refinement results for X-ray incident energy of 12000 eV and using the model 1 for the occupancy.

M2: 6500 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.128 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.45/0.55	0	0	0.403 (2)	0.05
M(3) Mn/Ti	3a	0.1/0.9	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05

a = b = 5.690 (5) $\text{\AA}$, c = 27.90 (4) $\text{\AA}$, R_{wp} = 33.8%, R_{exp} = 15.84%, Chi^2 = 4.55

Table 2.9: Refinement results for X-ray incident energy of 6500 eV and using the model 2 for the occupancy.

M2: 6535 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.45/0.55	0	0	0.402 (2)	0.05
M(3) Mn/Ti	3a	0.1/0.9	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05

"a = b = 5.688 (5) $\text{\AA}$, c = 27.89 (3) $\text{\AA}$, R_{wp} = 32.8%, R_{exp} = 15.43%, Chi^2 = 4.53"

Table 2.10: Refinement results for X-ray incident energy of 6535 eV and using the model 2 for the occupancy.

M2: 6564 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.45/0.55	0	0	0.402 (3)	0.05
M(3) Mn/Ti	3a	0.1/0.9	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05

"a = b = 5.687 (6) $\text{\AA}$, c = 27.89 (4) $\text{\AA}$, $R_{\text{wp}} = 38.7\%$, $R_{\text{exp}} = 22.43\%$, $\text{Chi}^2 = 2.98$ "

Table 2.11: Refinement results for X-ray incident energy of 6564 eV and using the model 2 for the occupancy.

M2: 12000 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.2856 (3)	0.55 (2)
Ba(2)	6c	1.0	0	0	0.1286 (3)	0.22 (2)
M(1) Mn	3b	1.0	0	0	0.5	0.15 (4)
M(2) Mn/Ti	6c	0.45/0.55	0	0	0.4070 (8)	0.35 (4)
M(3) Mn/Ti	3a	0.1/0.9	0	0	0	0.50 (4)
O(1)	18f	1.0	0.149 (5)	0.851 (5)	0.457 (2)	0.13 (9)
O(2)	18f	1.0	0.155 (6)	0.845 (6)	0.629 (2)	0.10 (9)

a = b = 5.6934 (3) $\text{\AA}$, c = 27.922 (2) $\text{\AA}$, $R_{\text{wp}} = 17.8\%$, $R_{\text{exp}} = 7.90\%$, $\text{Chi}^2 = 5.19$

Table 2.12: Refinement results for X-ray incident energy of 12000 eV and using the model 2 for the occupancy.

M3: 6500 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.128 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.4/0.6	0	0	0.403 (2)	0.05
M(3) Mn/Ti	3a	0.2/0.8	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05

a = b = 5.690 (5) $\text{\AA}$, c = 27.90 (4) $\text{\AA}$, $R_{\text{wp}} = 33.8\%$, $R_{\text{exp}} = 15.84\%$, $\text{Chi}^2 = 4.55$

Table 2.13: Refinement results for X-ray incident energy of 6500 eV and using the model 3 for the occupancy.

M3: 6535 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.4/0.6	0	0	0.402 (2)	0.05
M(3) Mn/Ti	3a	0.2/0.8	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05

"a = b = 5.688 (5) $\text{\AA}$, c = 27.89 (3) $\text{\AA}$, R_{wp} = 32.8%, R_{exp} = 15.43%, Chi^2 = 4.53"

Table 2.14: Refinement results for X-ray incident energy of 6535 eV and using the model 3 for the occupancy.

M3: 6564 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.286 (1)	0.05
Ba(2)	6c	1.0	0	0	0.129 (1)	0.05
M(1) Mn	3b	1.0	0	0	0.5	0.05
M(2) Mn/Ti	6c	0.4/0.6	0	0	0.402 (3)	0.05
M(3) Mn/Ti	3a	0.2/0.8	0	0	0	0.05
O(1)	18f	1.0	0.151	0.849	0.457	0.05
O(2)	18f	1.0	0.167	0.833	0.627	0.05

"a = b = 5.687 (6) $\text{\AA}$, c = 27.89 (4) $\text{\AA}$, R_{wp} = 38.7%, R_{exp} = 22.43%, Chi^2 = 2.98"

Table 2.15: Refinement results for X-ray incident energy of 6564 eV and using the model 3 for the occupancy.

M3: 12000 eV						
Atom	Site	Occupancy	x	y	z	Biso ($\text{\AA}^2$)
Ba(1)	6c	1.0	0	0	0.2856 (3)	0.56 (2)
Ba(2)	6c	1.0	0	0	0.1286 (3)	0.22 (2)
M(1) Mn	3b	1.0	0	0	0.5	0.15 (4)
M(2) Mn/Ti	6c	0.4/0.6	0	0	0.4070 (8)	0.35 (4)
M(3) Mn/Ti	3a	0.2/0.8	0	0	0	0.50 (4)
O(1)	18f	1.0	0.149 (5)	0.851 (5)	0.457 (2)	0.13 (9)
O(2)	18f	1.0	0.155 (6)	0.845 (6)	0.629 (2)	0.10 (9)

a = b = 5.6934 (3) $\text{\AA}$, c = 27.922 (2) $\text{\AA}$, R_{wp} = 17.8%, R_{exp} = 7.90%, Chi^2 = 5.16

Table 2.16: Refinement results for X-ray incident energy of 12000 eV and using the model 3 for the occupancy.

Chapter 3

Thermodynamics and Magnetism

Thermodynamic and macroscopic magnetic data are paramount to characterize the system state in the low temperature region. It is particularly important to detect the existence of a phase transition, or its absence.

In order to extract information about the magnetic interactions, it is important to be able to model such results theoretically. For this purpose, I begin this chapter summarizing the theory for magnetic interactions. Thereafter, I explain the two possible different counting for magnetism in this material used in the magnetic susceptibility and magnetic entropy models.

All raw data contained in this chapter was measured by Prof. Dr. Rafael Sá de Freitas, and the data treatment and analysis was performed by myself.

3.1 Theory of Exchange interaction

In localized magnetism, the electrons are in the atoms orbitals, giving such atoms a resultant spin. When one says, for example, that Mn^{4+} has $S = 3/2$, it means that the electronic configuration of Mn in this material results in an effective $S = 3/2$.

When the interaction between the electrons and their respective spins (or ions and its effective spins) is treated with quantum mechanical theory, it gives origin to the *exchange interaction*.

The exchange interaction is a spin-spin interaction that arises from the Pauli exclusion principle applied to the calculation of the Coulomb interaction. The spin dependent term results in a Hamiltonian described in equation 3.1, with J as the exchange constant, in units of energy.

$$\mathcal{H} = JS_1.S_2 \quad (3.1)$$

When all the neighboring spins are considered, this equation takes the form of *Heisenberg Hamiltonian*:

$$\mathcal{H} = \sum_{i < j} J_{ij} \mathbf{S}_i . \mathbf{S}_j \quad (3.2)$$

where $J > 0$ implies in an antiferromagnetic ground state to minimize the energy, and $J < 0$ corresponds to a ferromagnetic ground state.

3.1.1 Superexchange interaction

The concept of superexchange interaction is in contrast with the concept of *direct interaction*. The direct interaction is the exchange interaction resulting from the overlap between the atomic orbitals of two nearby orbitals. However, this type of interaction is not very effective for rare earth and transition metals, since their orbitals are very localized and thus the overlap of the orbitals is not significant.

With this in mind, the mechanism behind interactions for most relevant magnetic materials is not direct, but indirect, happening in the form of the *superexchange interaction*.

The superexchange interaction is defined as an interaction between two magnetic ions mediated by a non-magnetic ion in the middle of the other two. It is an indirect exchange mechanism and occurs because it is energetically favorable to couple the magnetic ions with a certain orientation for their interaction.

Usually, superexchange can be observed in transition metal ions mediated by oxygen. The most basic illustration of this process is: the oxygen has two p electrons, which have its spins align antiparallel. When the d orbitals from the transition metal hybridize with the oxygen p orbitals, the spin from each transition metal couples antiparallel with each oxygen electron, giving origin to an effective antiferromagnetic interaction between the spins of the transition metal atoms.

To calculate the exchange theoretically, second-order perturbation theory must be used [39]. In this thesis, it will be treated phenomenologically.

3.2 Thermodynamic and magnetic data modeling

Our first step is to apply a microscopic model to describe the system's susceptibility in order to extract the high temperature energy scales J_1 and J_2 . These interaction constants are related to the first and second neighbors physics within the structural trimers, as explained in the Introduction. Then, the low temperature magnetic specific heat data will be analyzed to characterize the magnetic behavior at this temperature region.

The results of both J_1 and J_2 will also be important in the analysis of the specific heat data and in the determination of the ground states of the highly correlated magnetic dimers and trimers. The energy scales related to the ground and first excited states are important to understand which are the remaining magnetic degrees of freedom in the system.

The formation of structural trimers and its different possibilities of occupations (as discussed in Chapter 2 and shown in Figure 1.5) give rise to three different types of magnetic specimens in the system: magnetic trimers, magnetic dimers and orphan spins. The former two specimens are

highly correlated states that are coupled by superexchange interactions between the Mn cations, mediated by the oxygen octahedron. The orphan spin is a single spin, interacting with a mean field molecular field.

In the structural trimers, the Mn sites are inside face-sharing octahedra of coordinating oxygen atom. This gives rise to a large multiplicity of exchange paths, mediated by the oxygen, which is the cause of superexchange between the Mn cations which is implied to be large.

There are two different ways of counting the fractions of each magnetic specimens per mol of Mn: the ordered counting and the disordered counting. This happens because we can have a statistical filling of site Mn(2) which gives rise to magnetic dimers for half of the structural trimers, which is the *disordered counting*. Or we can have each structural trimer in the unit cell as a different magnetic specimen, resulting in only one third of magnetic dimers, which is a ordered unit cell with mixed occupancy and will be called *ordered counting*. The order and disorder here refers to the position of trimers, dimers and orphans along the material. Both counting are explained bellow.

3.2.1 Ordered counting

The unit cell of our system contains 12 formula unit and thus 12 transition metal sites (as shown in the site multiplicity in Table 2.1), from which half are occupied by Mn. 9 of these sites form 3 structural trimers.

The fraction of magnetic trimers, dimers and orphans spins in the structure, follows from the different ways to fill the M(2) site in the structural trimer, taking into account the number of sites in the unit cell. The site filling within a unit cell is:

- 3 M(1) sites filled with Mn;
- 6 M(2) sites, 3 filled with Mn and 3 filled with Ti;
- 3 M(3) sites filled with Ti (which do not participate in the structural trimer).

Following this counting, each unit cell (containing 6 Mn) has one magnetic trimer, one dimer and one orphan Mn. Thus, out of each mol of Mn there are 1/6 mol of magnetic trimers, magnetic dimers and orphan spins. This fraction is halved when a mol of substance is considered.

3.2.2 Disordered counting

The difference here lies in the treatment of the M(2) site filling over the material. When one thinks statistically about it, the filling of both M(2) sites in the structural trimer is: half of the upper M(2) sites in the structural trimer being Mn and half being Ti, the same happening to the lower M(2) site. It would form a dimer half of the times and a magnetic trimer and a orphan

spin with 1/4 chance each. So, for each 8 Mn, 3 would be in a magnetic trimer (forming 1 trimer), 4 in two magnetic dimers (forming 2 dimers) and 1 in an orphan spin. Therefore, per mol of Mn, we would have 1/4 mol of magnetic dimers and 1/8 mol of magnetic trimers and orphan spins.

3.3 Magnetic Susceptibility

Since the magnetic susceptibility is an accessible technique, it is usually the first data to consider to characterize the existence of phase transition, and therefore, as an evidence for a strong magnetic frustration in a system.

The magnetic susceptibility was measured for temperatures as low as 0.5 K using a SQUID (Superconducting Quantum Interference Device) magnetometer for $2 \leq T \leq 300$ K and a VSM (Vibrating Sample Magnetometer) to lower temperatures. The data is presented in Figure 3.1.

In the high temperature paramagnetic region, the magnetic susceptibility of all magnetic systems are expected to follow Curie-Weiss law, given by equation 1.1. Following this model, it is expected that some non-analyticity would appear in a system with a phase transition. This is not visible for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ in Figure 3.1, on the contrary, what is observed is a smooth trend toward saturation in the low temperature limit, as observed in the upper right insert, which is an indication that the spins are correlated but not ordered.

Figure 3.1: Magnetic susceptibility ($\chi(T)$) data as a function of T ($0.6 \leq T \leq 330$ K). The red line represents the data fitted to the model in equation 3.8. The insert shows $\chi(T)$ for $T < 12$ K.

However, the Curie-Weiss law is based on systems with one type of magnetic unit. That is not the $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ case. Here, as already discussed, we have magnetic trimers, magnetic dimers and orphan spins, and the two former units are related to strong local exchange couplings.

For the case of the orphan spins magnetic susceptibility χ_{orp} , it is directly derived from the Curie-Weiss model in equation 3.3, where χ_0 corresponds to a diamagnetic response and is expected to be negligible.

$$\chi_{\text{orp}}(T) = \frac{C_{\text{orp}}}{T - \theta_{\text{orp}}} + \chi_0 \quad (3.3)$$

It is possible to calculate the magnetic susceptibility and specific heat for a trimer and a dimer using the corresponding Hamiltonian, defined in equation 3.4, where J_1 is the superexchange interaction constant between the nearest Mn and J_2 is the superexchange interaction constant between the second nearest Mn. The latter is only present in the case of a magnetic trimer. Both interaction constants are in units of Kelvin. $\mathbf{S}_n$ refers to spin $n = 1, 2, 3$ interacting with each other. $\mathbf{H}$ is the magnetic field, μ_B is the Bohr magneton, k_B is the Boltzmann constant and g_J is the Landé g-factor, defined by equation 3.5 [39].

$$\begin{aligned} \mathcal{H}_{\text{dim}} &= J_1 \mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{g_J \mu_B}{k_B} (\mathbf{S}_1 + \mathbf{S}_2) \cdot \mathbf{H} \\ \mathcal{H}_{\text{trim}} &= J_1 \mathbf{S}_1 \cdot \mathbf{S}_2 + J_1 \mathbf{S}_2 \cdot \mathbf{S}_3 + J_2 \mathbf{S}_1 \cdot \mathbf{S}_3 + \frac{g_J \mu_B}{k_B} (\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3) \cdot \mathbf{H} \end{aligned} \quad (3.4)$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (3.5)$$

Writing the $S = 3/2$ spins as 4×4 matrices, their coupling (or direct product) will be a 16×16 matrix, with 16 eigenvalues. This way, it is possible to compute the partition function with a sum over the eigenvalues.

The magnetization can be written as a function of the partition function as expressed in equation 3.6. From this, we can calculate the magnetic susceptibility, which will be in units of energy x temperature x field⁻².

$$M = -\frac{\partial F}{\partial H} = T \frac{\partial \ln Z}{\partial H} \quad (3.6)$$

$$\chi = \frac{\partial M}{\partial H} = -\frac{\partial^2 F}{\partial H^2} \quad (3.7)$$

In this analysis, the resulting magnetic susceptibility $\chi(T)$ will be the relative sum of the terms $\chi_{\text{trim}}(T)$, $\chi_{\text{dim}}(T)$ and $\chi_{\text{orp}}(T)$ referring to the proportional population of orphans, dimers and trimers, respectively, per mol of substance, as in equation 3.8, where N_a is the Avogadro constant and the f are the fraction of orphan, dimer and trimers per mol of substance, accord-

ingly with the ordered (all $f = 1/12$) or disordered counting ($f_{\text{orp}} = f_{\text{tri}} = 1/16$, $f_{\text{dim}} = 1/8$). The data is in units of emu/mol.Oe.

$$\chi(T) = N_a(f_{\text{orp}}\chi_{\text{orp}}(T) + f_{\text{dim}}\chi_{\text{dim}}(T) + f_{\text{tri}}\chi_{\text{trim}}(T)) \quad (3.8)$$

With the use of the software *Mathematica* [40], the total magnetic susceptibility was calculated and the model was fitted to the data in the region $T > 5.5$ K. The fitting is in Figure 3.1, as a red line. However, one approximation was used: to consider the eigenvalues to be linear with the field $\mathbf{H}$, making the derivative in $\mathbf{H}$ of the eigenvalues to be a constant.

Considering the ordered counting, the fitting results are the values of $J_1 = 175(5)$ K, $J_2 = 0.58(5)J_1$, $\theta_{\text{orp}} = -7.3(3)$ K, $C_{\text{orp}} = 0.12(1)$ emu.K/mol(f.u.).Oe and $\chi_0 = 0.00011(5)$ emu/mol(f.u.).Oe. It is summarized in Table 3.1.

Calculating from eq. 1.2, the expected value for the Curie constant in a spin $S = 3/2$ system with $1/12$ mol of spins is $C \approx 0.15$ emu.K/mol(f.u.).Oe. This values agrees with the one from the fitting in some extent. But taking into account the complexity of the system and the approximations made, it is a good agreement.

From the values $J_1 = 175(5)$ K and $J_2 = 0.58J_1$ it is possible to model the trimer system and calculate its ground state: an effective $S = 1/2$ resulting from the sum of the three $S = 3/2$, with the first excited state lying at $T \approx 30$ K above the ground state. Knowing the ground state is very important to model and understand the spin system at low temperatures, as well to propose an emerging magnetic lattice.

In the low temperature region, with the large value of the exchange interaction J_1 , the dimers will form a singlet state (non degenerate ground state) and will be, therefore, frozen for the magnetism, not contributing to the low temperature magnetic dynamics. This way, the low temperature magnetic degrees of freedom will be formed by $S = 3/2$ orphan spins and effective $S = 1/2$ spins from the magnetic trimer. The interaction between these remaining magnetic degrees of freedom can be modeled by a mean field approximation, that means a Curie-Weiss interaction model.

The Curie-Weiss temperature for the magnetic trimer and orphan spin effective interaction is $\theta_{\text{orp-trim}} = -8.5(5)$ K and the Curie constant is $C_{\text{orp-tri}} = 0.19(1)$ emu.K/Oe.mol(f.u.). Since no phase transition is observed down to 0.1 K, the frustration factor lower bond is of about $f \approx 85$.

From eq. 1.2, we can calculate the expected Curie constant for a population of $1/12$ mol of $S = 1/2$ and $1/12$ mol of $S = 3/2$, interacting by a mean field:

$$C_{\text{orp-tri}} = \frac{1}{12} \times g^2 \mu_B^2 \frac{(1/2 \times (1/2 + 1) + 3/2 \times (3/2 + 1))}{3k_B} \approx 0.18 \quad (3.9)$$

in units of emu.K/Oe.mol(f.u.). The gyromagnetic ratio was taken as $g = 2$, assuming no orbital contribution to the total spin. Therefore, the experimental Curie constant compares well with the predicted value.

Fitting the magnetic susceptibility for the disordered counting, the parameters obtained are as follows: $J_1 = 176(7)$ K, $J_2 = 0.59J_1$, $\theta_{\text{orp}} = -6.8(2)$ K and $C_{\text{orp}} = 0.13(1)$ emu.K/Oe.mol (f.u.). The numbers are slightly different than the ones for the ordered counting, and are compared in Table 3.1. Now, the value of $C_{\text{orp}} = 0.13(1)$ emu.K/Oe.mol (f.u.) must be compared with $C \approx 0.12$ emu.K/Oe.mol (f.u.) expected for $1/16$ mols of Mn $S = 3/2$ spins (orphan spins) per formula unit of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ (half mol of Mn), which is a good agreement. Since the exchange interaction values are practically the same, the interpretation and energy scales for the ground state formation of magnetic dimers and trimers is unchanged. The fitting also gives the values of $\theta_{\text{orp-tri}} = -7.5(1)$ K, given a frustration parameter f of at least $f \approx 75$, and a resulting Curie constant $C_{\text{orp-tri}} = 0.18(1)$ emu.K/Oe.mol (f.u.) which compares well with the expected ≈ 0.14 emu.K/Oe.mol (f.u.), as shown in equation 3.10.

$$C_{\text{orp-tri}} = \frac{1}{16} \times g^2 \mu_B^2 \frac{(1/2 \times (1/2 + 1) + 3/2 \times (3/2 + 1))}{3k_B} \approx 0.14 \quad (3.10)$$

	Ordered		Disordered	
	Fitting	Theory	Fitting	Theory
J_1 (K)	175(5)		176(5)	
J_2/J_1	0.58(5)		0.59(5)	
θ_{orp} (K)	-7.3(3)		-6.8(2)	
C_{orp} (emu.K/mol (f.u.).Oe)	0.12(1)	0.15	0.13(1)	0.12
χ_0 (emu/mol(f.u.).Oe)	0.00011(5)		0.00036(4)	
$\theta_{\text{orp-tri}}$ (K)	-8.5(5)		-7.5(5)	
$C_{\text{orp-tri}}$ (emu.K/mol (f.u.).Oe)	0.19(1)	0.18	0.19(1)	0.14

Table 3.1: Fitting values from the magnetic susceptibility model, using the two different counting for the fraction of trimers, dimers and orphan spins.

Examining these results, the susceptibility does not offer an answer to which of the counting describes better the material, giving no considerable difference between the two fractions.

Another set of experimental data concerning the magnetic susceptibility is the AC susceptibility. AC magnetic susceptibility measurements (χ') consists of a measurement of magnetic susceptibility under an applied field that varies sinusoidally, with a fixed frequency. This is in contrast with DC susceptibility, where the applied magnetic field is constant.

With the use of AC susceptibility, it is possible to visualize some consequences of the spin dynamics in the material. If the material presents a magnetic ordered state with short correlation distances, such a spin glass, some time depended oscillation will appear in the $\chi'(T)$ measurement for temperatures lower than the spin glass transition temperature. This occurs as a consequence of many different timescales involved in the freezing process.

Also, if a phase transition is present in the DC susceptibility, it is expected that it will change with frequency in the AC susceptibility.

Given these observations, we can turn our attention to the AC magnetic susceptibility data

in Figure 3.2. For $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ the AC magnetic susceptibility does not present any oscillations with applied field for frequencies between 1 Hz and 1000 Hz. Also, the data does not show any sign of transition and it is completely frequency independent.

Figure 3.2: AC Susceptibility ($\chi'(T)$) measurements as a function of T ($1.8 < T < 300$ K) at distinct frequencies.

Accordingly, it is safe to assume that no sign of a spin glass transition for temperatures as low as 1.8 K is present in the AC susceptibility data, which support the thesis that the system presents a spin liquid ground state. If a spin glass transition occurs, a frequency dependency would appear below such transition. Thus, a spin glass ground state could only be present if its frozen temperature is below 1.8 K.

3.4 Magnetization

The isothermal magnetization was measured for $T = 0.6$ K and magnetic field up to 10 T using the VSM. The data is presented in Figure 3.3.

As observed, the magnetization seems to be far from saturation even in the presence of fields of about 10 T.

Figure 3.3: Isothermal magnetization ($T = 0.6$ K) as a function of H ($M(H)$).

3.5 Specific Heat

The specific heat was measured for temperatures as low as 0.1 K for different magnetic field values, up to 9 T, using a PPMS (*Physical Property Measurement System*) from Quantum Design.

The data is presented in Figure 3.4. This specific heat is a sum of lattice contribution with magnetic contribution, which can be very difficult to separate. However, the magnetic specific heat is a very crucial experiment to observe spin liquid behavior, or any highly frustrated magnetic phase.

It is possible to see a large dependency of the data as a function of the magnetic field in the lower temperature region. At around 5 K it is possible to see a change of pattern of the field dependency. This region, as the μ SR data will make very clear, is a crossover region, where the system changes its magnetic dynamics from one behavior to another completely different.

In order to subtract the lattice contribution, it is important to keep in mind that this contribution can be neglected in the lowest temperature region. However, it becomes progressively relevant with increasing temperature.

One possible way to subtract the lattice contribution is to find an analogous non magnetic lattice and subtract its specific heat from the sample data. At the present, the best reference lattice is provided by barium titanate BaTiO_3 [41], from which the $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ is derived. The BaTiO_3 specific heat is compared with $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ for zero field in Figure 3.5.

Figure 3.4: specific heat ($C_p(T)$) data as a function of T and applied magnetic field H .

Figure 3.5: $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ specific heat data ($H=0$) compared with the BaTiO_3 specific heat.

Following the subtraction of this model lattice contribution, the magnetic contribution to the

specific heat (abbreviated (C_{mag})) are presented in Figure 3.6. The same subtraction for zero field is made on all data, since the phonon contribution does not depend on the applied field. It is possible to observe that the curve changes substantially as a function of magnetic field.

Figure 3.6: Magnetic specific heat ($C_{\text{mag}}(T)$) after the lattice contribution of Figure 3.5 subtraction.

In a close inspection of the lowest temperature magnetic specific heat, it is possible to observe that some upturn is present in the data. One can wonder if this is due to a phase transition, namely, a magnetic ordering. However, it is more plausible that this upturn is due to the nuclear magnetism from the Mn ions.

As shown in Figure 3.7, it is possible to compare the zero field low temperature specific heat (or magnetic specific heat, since the lattice contribution is negligible for $T < 2$ K) to the specific heat of another model sample, MnNi [42]. For the region $T < 0.2$ K, the MnNi specific heat is mainly due to nuclear degrees of freedom and agrees well with our data. Therefore, it is evidence that no phase transition is observed down to $T \approx 0.1$ K in the specific heat.

Figure 3.7: Nuclear specific heat of MnNi in contrast with the low temperature specific heat of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$

The specific heat in the region $0.3 < T < 1$ K is practically unaffected by the BaTiO_3 and MnNi subtractions. Therefore, the specific heat in this region can be considered equal to the magnetic specific heat of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ interacting spin system, and can be used to fit a power law as defined in equation 3.11, where γ and α are field dependent parameters of this magnetic phase. The power law behavior is characteristic of spin liquid phases.

$$C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)} \quad (3.11)$$

The resulting fittings are shown in Figure 3.8, and the corresponding field dependent parameters are shown in Figure 3.9. The $\alpha(H)$ parameter can be considered constant at around ≈ 1.4 , taking into account the error bars, suggesting gapless excitations of the spin state. Given the fact that $\alpha(H) > 1$ and therefore $C_{\text{mag}}(T)/T$ does not diverge with $T \rightarrow 0$, it is possible to conclude that the system is far from quantum criticality [43], which means that the magnetic entropy of the system will not diverge in the zero temperature limit. Additionally, the $\gamma(H)$ parameter decreases from ≈ 0.45 at $H = 0$ T to ≈ 0.25 J/mol(Mn)K $^\alpha$ at $H = 9$ T as the field increases, resulting in a quenching of the magnetic entropy as a function of the field.

Figure 3.8: Magnetic specific heat fitting in the low T region ($0.3 < T < 1.0$ K) to the expression $C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)}$ for different values of H .

Figure 3.9: $\alpha(H)$ and $\gamma(H)$ parameters from the fitting in Figure 3.8.

3.5.1 Zero Field Magnetic Entropy

The expected magnetic entropy of the ground state is due to the remaining magnetic degrees of freedom of the compound at the lowest temperatures, including: the trimer ground state, which is an effective $S = 1/2$ spin, and orphan $S = 3/2$ spins. At zero field these ground states are degenerated, because the possible spin orientations have the same energy. This gives origin to a non zero entropy associated with the ground states of trimers and orphan spins, which is possible to calculate as shown in equation 3.12, for the ordered counting, or equation 3.13 for disordered counting.

$$\Delta S = R(\ln 4 + \ln 2)/6 = 1.92 + 0.96 = 2.88 \quad (3.12)$$

$$\Delta S = R(\ln 4 + \ln 2)/8 = 1.44 + 0.72 = 2.16 \quad (3.13)$$

With the use of the magnetic specific heat for zero field, we can obtain experimentally the magnetic entropy of the system in the zero temperature limit and compare it with these predicted values. To do this, however, for the temperature region $T < 0.3$ K, instead of using the magnetic specific heat data as shown in Figure 3.6, which contains the Mn magnetic nuclear contribution, we use the fitting parameters in Figure 3.9 to extrapolate the magnetic specific heat for this region.

In short, we use the fitting of the specific heat made for the region $0.3 < T < 1.0$ K to calculate the specific heat for temperatures between 0.01 K and 0.3 K. With it, the magnetic entropy is calculated directly from the magnetic specific heat, as shown in equation 3.14 and figure 3.10.

$$\Delta S = \int_{0.01}^{9.81} \frac{C_{\text{mag}}}{T} dT = 1.97 \quad (3.14)$$

Comparing the experimental value with the predicted ones, the recovered magnetic entropy value of 1.97(5) J/K.mol(Mn) corresponds to about 2/3 of the expected for the ordered counting, closely only to the orphan spins expected entropy. And it corresponds to about 91% of the expected for the disordered counting, suggesting that the remaining magnetic degrees of freedom must include $S = 3/2$ and effective $S = 1/2$ spins in this case.

This means that not all the entropy is recovered in the low temperature region and some residual entropy is still present in the system in the lowest temperature region for both counting.

Maybe the calculated value is wrong because the trimer is not participating in the low temperature magnetic state, which raises the question: do the magnetic trimers achieve magnetic order? If this were the case, the trimers would not participate in the magnetic entropy, they would be ordered and some non-analicity would appear in the magnetic susceptibility, as well as field dependent Schottky anomalies in the specific heat. As will be shown below in our investigation, Schottky anomalies are not present in the data.

Figure 3.10: Magnetic specific heat for zero field and the corresponding magnetic entropy $\Delta S(T)$. For the region $0.01 < T < 0.3$ K the data is calculated from the fitting shown in Figure 3.8.

3.5.2 Schottky anomaly calculation

To support the previous statement concerning the participation of trimers in the low temperature magnetic state, the software *Mathematica* was used to calculate the expected Schottky anomaly for the dimers and trimers. The Schottky anomaly is an effect in the specific heat that manifests as a broad peak. It occurs in systems with discrete energy levels, indicating that there are a small number of energy levels dominating the behavior of the system [39].

The calculation is based on the assumption that the magnetic dimers and trimers have interactions only within the structural trimer, and consequently, the magnetic dimers and trimers do not interact with each other at low temperatures, thus, are magnetically isolated and do not contribute to the low temperature magnetism. As we will see, this assumption does not explain the data and therefore, it supports that the magnetic trimers indeed interact with each other and are present in the low temperature magnetic state.

Given the experimentally determined values of $J_1 = 175(5)$ K e $J_2 = 0.58J_1$, it is possible to calculate all eigenvalues for the dimer and trimer interaction systems. With it, the magnetic specific heat would be as defined in equation 3.15. Moreover, the results were normalized for units of J/K.Mol(Mn) with the fractions of Mn atoms forming trimers and dimers as discussed in the beginning of this chapter.

$$C_{\text{mag}} = \frac{\partial}{\partial T} \sum_n E_n \exp(-E_n/k_B T) \quad (3.15)$$

The dimer is a system with two $S = 3/2$ spins interacting under an exchange constant of $J_1 = 175(5)$. The trimer is a system with three $S = 3/2$ spins interacting with first neighbors exchange constant of $J_1 = 175(5)$ and second neighbors exchange constant of $J_2 = 0.58J_1$. Both systems can be under the effect of an external magnetic field, that is, a Zeeman term in the Hamiltonian.

Figure 3.11: Calculated magnetic specific heat for the dimer system. The result is field independent and negligible in the low temperature limit.

The resulting magnetic specific heat and its magnetic field dependency is presented in Figure 3.11 and 3.12. For the dimers, it results in a coupled spin with effective spin zero (a singlet) for the temperature region considered. For the trimer, it results in a ground state with effective spin of $S = 1/2$ for zero field. The Schottky appears under influence of the magnetic field.

Since the dimer contribution is practically zero for $T < 15$ K, we can compare the experimental magnetic specific heat with the trimer contribution, as shown in Figure 3.13 for $H = 1$ T and $H = 9$ T. The trimer contribution alone would be larger than the total magnetic specific heat. From this comparison, we have evidence that the trimers indeed are not magnetically isolated from each other, that means, the trimer system are forming a lattice of correlated trimers, which prevents Schottky anomalies from showing in the magnetic specific heat.

Furthermore, our calculations explain that the dimers do not contribute to the previously

Figure 3.12: Calculated magnetic specific heat for the trimer system. The result is field dependent and Schottky anomalies appear with the influence of an external magnetic field.

discussed residual entropy calculation, since the recovery of the dimer entropy occurs at higher temperatures.

Figure 3.13: Comparison between the calculated trimer Schottky anomaly and experimental data for $H = 1 \text{ T}$ and $H = 9 \text{ T}$.

Chapter 4

Microscopic Measurements

Microscopic probes are crucial to the characterization of highly frustrated magnetic phases. Due to the absence of long range order, the local correlations in the magnetic ions sites must be detected using this kind of probe.

It is known that spin liquids shows collective spin excitations, which translates into correlation between spins in the low temperature region [21, 12]. This dynamic can be probed using Muon Spin Resonance (μ SR).

4.1 Muon Spin Resonance (μ SR)

The Muon Spin Resonance (μ SR) technique, also known as muon spin rotation or relaxation, is essential to characterize the continuous magnetic excitations in the material in order to obtain experimental evidence that a collective spin state is formed in the low temperature regime.

For this purpose, a beam of polarized muons is implanted in a sample and is subjected to its local internal fields. The muon, which is a spin-1/2 particle, will begin to precess in the presence of the local magnetic field. Since the muon momentum is fixed for a given spin direction, the precession will be responsible for an asymmetry in the detected muons considering the initial polarization axis. That asymmetry is what is measured, making the muon act as a microscopic magnetometer [44].

4.1.1 Muon production, implantation and detection

In order to produce a beam of polarized muons (μ^+), a high energy proton beam is fired into a graphite target to produce pions (π^+): the decay of two protons will generate a pion, a proton and a neutron as shown in equation 4.1. The pion will decay into a muon and its respective neutrino (ν_μ), which is shown in equation 4.2. This is the muon that hits the sample, in a beam that is spin-polarized due to conservation of momentum. Thus, the muon will have

its polarization aligned antiparallel to its spin: the beam of muon hits the target pointing in the opposite direction to its propagation.

$$p + p \rightarrow \pi^+ + p + n \quad (4.1)$$

$$\pi^+ \rightarrow \mu^+ + \nu_\mu \quad (4.2)$$

After it is implanted in the sample, each muon will be subjected to precess in the presence of the local fields. However, the lifetime of these muons is $2.2 \mu\text{s}$: each muon will decay into a positron (e^+), its respective neutrino (ν_e) and a muon antineutrino ($\bar{\nu}_\mu$), as shown in equation 4.3.

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu \quad (4.3)$$

The emitted positron emerges with spin predominantly along the direction of the muon spin, thus, it reflects the coupling of muon with the local fields.

To detect the positron spin, it is deflected by a detection magnetic field, in order to hit either one of two different detectors, depending on its momentum. This will lead to a counting in each detector that reflects the spin of the implanted muon. This is summarize in the Asymmetry function, defined in equation 4.4, where $N_B(t)$ is the positron counting in the backward detector and $N_F(t)$ the counting in the forward detector. The backward and forward detectors are placed in front and behind the sample, along the beam axis. Since the decay process is radioactive, $N_B(t)$ and $N_T(t)$ will actually decay exponentially. The asymmetry function use the normalized values for the detector counting.

$$A(t) = \frac{N_B(t) - N_F(t)}{N_B(t) + N_F(t)} \quad (4.4)$$

Consequently, the asymmetry function can be related to the time evolution of the muon spin polarization.

In Zero Field (ZF) experiments, the only field in which the muon can precess is the internal field in the sample. If the sample is polycrystalline and has magnetic long-range order, the precession will always occur, giving origin to an oscillatory behavior in the asymmetry function. If the sample is monocrystalline, the internal fields will cause precession, unless they are parallel to the muon polarization.

Longitudinal Field (LF) experiments have an applied magnetic field parallel to the muon polarization, not giving origin to a precession process, but to a relaxation regime.

4.1.2 μSR data and analysis for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$

The μSR data for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ was taken by Fernando Assis Garcia in the line πM3 of the Paul Scherrer Institute (PSI) localized in Villigen, Switzerland. With the use of the

Figure 4.1: μ SR spectra for zero field in the crossover region ($1.5 < T < 10$). The lines are fittings to the stretched exponential of equation 4.5. All data is from GPS spectrometer.

spectrometers GPS (General Purpose Surface-Muon Instrument) and LTF (Low Temperature Facility Instrument) a wide range of temperatures was accessed: the measurements were performed for temperatures in the interval $0.019 < T < 10$ K (LTF) and $1.5 < T < 200$ K (GPS) for zero field (ZF) and longitudinal field (LF) applied up to 0.05 T. The longitudinal field is parallel to the initial polarization of incident muons. In the LFT spectrometer the sample was glued to a Ag plate, in order to improve the thermal contact. This gives origin to a background in the asymmetry function which does not depend on temperature or time. All μ SR spectra were analyzed using the MUSRFIT software [45].

The figures 4.1 and 4.2 show some of the zero field (ZF) spectra. For temperatures as low as $T = 0.019$ K the spectra has exponential behavior, thus it does not show damped oscillations typical of a magnetically ordered phase [44, 46]. In Figure 4.1, it is possible to see that the spectra changes substantially in the region $1.75 < T < 10.5$ K, while in Figure 4.2 below $T = 1.5$ K the spectra is nearly temperature independent, showing similar behavior in the whole temperature interval.

This can be better observed when we adjust the asymmetry profile to the theoretical curve of a stretched exponential:

$$A(t) = A_0 \exp -(\lambda t)^\beta + B, \quad (4.5)$$

where A_0 is the initial asymmetry, B is due to the constant background, λ is the relaxation

Figure 4.2: μ SR spectra for zero field in the lowest temperature region ($T < 1.5$ K). The line is the fitting of the $T = 0.019$ K data to the stretched exponential of equation 4.5, and is representative of all temperatures in the graph. All data is from LTF spectrometer.

rate in units of s^{-1} and β is the dimensionless stretching exponent.

The parameters of this fitting as a function of temperature are shown in Figure 4.3. It is possible to observe that for $T < 1.5$ K only one fitting is suitable to all temperatures. The same occurs for $T > 10$ K, where λ becomes independent of T . Indeed, taking this into account, as well as the fact that $\beta = 1$, we can relate this region to a paramagnetic phase.

Figure 4.3: Coefficients: relaxation rate λ and the exponent β as a function of temperature T for both GPS and LTF spectrometers.

Therefore, we can define the region where the spectra changes the most $1.5 < T < 10$ K as a crossover region, where the system goes from paramagnetic to another phase with $\lambda \approx 1.2\mu\text{s}^{-1}$ and $\beta \approx 0.5$. However, there is no evidence of magnetic order as discussed in chapter 3.

The value of $\beta \approx 0.5$ is well above $1/3$ that would be expected for the spin glass dynamics of simple systems, indicating the absence of static local fields [47, 44].

It is interesting to notice that the crossover region defined above coincides with the one observed in the specific heat of the figure 3.4. It shows an agreement between the interpretations of macroscopic and microscopic measurements. This crossover behavior can be related to a spin liquid ground state [48, 49, 50].

In Figure 4.4 we can observe the longitudinal field (LF) spectra for $T = 0.1$ K. This data can be compared with the Dynamical Kubo-Toyabe (DKT) theory, which was used to fit the zero field data. The DKT theory consists of an asymmetry function convoluted with a Gaussian distribution of internal fields of width ΔH . For zero field the asymmetry function is as defined in equation 4.6 [51, 52, 44]. The asymmetry function is derived from the time average integral of the precession. Under the presence of an applied longitudinal field, the time average will be field dependent. It also depends on the precession frequency.

$$A(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2)e^{-\Delta^2 t^2/2} \quad (4.6)$$

Since, for zero field, it is a good fit, we can use the same parameters for the data with applied field. By doing so, it is clear that the model does not represent the experimental data. If some static magnetism were present in this temperature region, a field of ≈ 5 mT would be enough to strongly reduce the relaxation, as shown in the blue line in Figure 4.4. However, in the experimental data, even a field 10 times stronger (green data) is not enough for this theoretically predicted reduction.

Figure 4.4: Asymmetry profile of the longitudinal field (LF) data for $T = 0.1$ K and different magnetic fields. The lines are the expected spectra in the DKT theory.

This occurs because the DKT theory predicts the spin dynamics in the low temperature region for static magnetism, where the local field in the presence of an external field would reduce its relaxation by a considerable amount. Thus, we can conclude that the relaxation regime of this system for $T = 0.1$ K is more dynamic than expected.

Turning our attention to the spin fluctuation rate ν , it is possible to identify two fluctuation regimes: temperatures below and above the crossover region. For $T > 10$ K, the system is paramagnetic and it is possible to estimate the rate according to equation 4.7 [48]:

$$\nu_{T>10\text{ K}} = zJS/h, \quad (4.7)$$

where we can extract the J value from $\theta_{\text{orp}} = z\frac{JS(S+1)}{3}$. Taking $z = 6$, that is the number of first neighbors in the emerging magnetic lattice, $\theta_{\text{orp}} = -7.3$ from chapter 3 and h is the Planck constant. It results in $J \approx 0.97$ K and, consequently, in $\nu_{T>10\text{ K}} = 7.4(1) \times 10^{10}$ Hz.

It is possible to calculate the width of the field distribution Δ using equation 4.8, where λ refers to the region above the crossover: $\lambda_{T>10\text{ K}} \approx 0.07\mu\text{s}^{-1}$. Taking the magnetic field as zero, we obtain $\Delta = 5.09 \times 10^7$ Hz.

$$\lambda(H) = \frac{2\nu\Delta^2}{\nu^2 + (\mu_0 H^2 \gamma_\mu)^2} \quad (4.8)$$

For the region below the crossover $T < 1.5$ K, the system is no longer a conventional paramagnet and the model to the relaxation is [49]:

$$\lambda(H) = 2\Delta^2\tau^x \int_0^\infty t^{-x} \exp(-\nu_{T<1.5\text{ K}}t) \cos(2\pi\mu_0\gamma_\mu Ht) dt \quad (4.9)$$

where τ is the early time cutoff, Δ is the field distribution width for the low temperature region, x is a critical exponent and ν is spin fluctuation rate. The $\lambda(H)$ values are from the LF experiments stretched exponential fittings, which were used to fit eq. 4.9. The obtained parameters are $x = 0.64(3)$, $2\Delta^2\tau^x = 0.8(1)$ Hz and $\nu_{T<1.5\text{ K}} = 3.7(6) \times 10^6$ Hz. In comparison with $\nu_{T>10\text{ K}}$, the spin fluctuation rate decrease is of about 4 orders of magnitude, without symmetry breaking. In Figure 4.5, we can see the $\lambda(H)$ values and the fitting. It is important to observe that a small number of points were used in order to do the fit, so one must be careful to rely on the resulting parameters. With this in mind, the result suggests long-time spin correlation at low temperature for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, which can be interpreted as an evidence of an entangled spin state in this temperature region.

Figure 4.5: The red circles are the relaxation rate λ for different values of magnetic field (H) for the LF data. The blue line refers to the fitting to the equation 4.9.

Chapter 5

Discussion, Summary and Conclusion

5.1 Emerging Magnetic Sub-lattice

Concerning the $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ lattice geometry and symmetry, it is important to clarify some points that help understand the proposed emerging magnetic sub-lattice:

- The first point we can raise from the experimental data is: the formation of orphan spins, magnetic dimers and trimers.
- The second point: the absence of evidence for the formation of a super-lattice, which gives us little freedom to fill the unit cell while maintaining its symmetry and periodicity across the crystal.
- Third point: the counting of orphan spins, magnetic dimers and trimers fractions in the material, as explained at the beginning of chapter 3.

Taking into account all these observations and the assumption that the unit cell is the same over the material, which implies in the ordered counting defined in section 3.2.2, we can assume that the three layers of structural trimers in the unit cell, as shown in Figure 1.4, do not mix the types of magnetic specimens. It means that if the top structural trimer is an orphan spin, the bottom or the middle one is forcibly a magnetic trimer. That leaves the other one as a magnetic dimer. So, inevitably, given the translational symmetry, the result will be layers in the order orphan-dimer-trimer or orphan-trimer-dimer. However, the dimers do not participate in the magnetic ground state, so the resulting low temperature magnetic lattice will be bi-layers of triangular lattices, containing orphan spins and magnetic trimers, interacting with each other, and isolated from the other bi-layers by a layer of magnetic dimers. This is illustrated in Figure 5.1.

In this resulting magnetic lattice we have effectively two layers of a triangular lattice. One of the lattice is composed by $S = 3/2$ orphan spins, and the other by effective $S = 1/2$ spins. These layers are displaced from the other: the center of one triangle lies above the vertex of the

other, as indicated in Figure 5.1 by the full yellow line (AB stacking). The lattice parameter of the triangular lattices is 5.691 Å, while the trimer-orphan distance is 9.868 Å.

Figure 5.1: Model of the proposed emerging magnetic lattice at low temperatures. The lattice parameter is 5.691 Å. The trimer-orphan distance is 9.868 Å, represented by the dashed yellow line. The full yellow line represents the displacement between the two planes. The oxygen atoms were omitted in the octahedra for the visualization.

However, this interpretation would imply the loss of symmetry of the unit cell, which would affect the resonant XRD diffraction pattern. The symmetry of the lattice would be a subgroup of the space group $R\bar{3}m$ with the loss of the -3 symmetry, which is a rotation of $2\pi/6$ followed by a reflection in relation to a plane perpendicular to the rotation axis. In this case, the ab plane. However, the resonant XRD confirms the $R\bar{3}m$ symmetry.

One possible arrangement, taking in consideration all discussed above, would be a unit cell with double the size in the c axis direction. In this way, the three structural trimers would be reflected in the second half of the new unit cell, maintaining the symmetry while doubling the unit cell. The new layers of structural trimers could then present the following arrangements of magnetic specimens: orphan-dimer-trimer-trimer-dimer-orphan, dimer-trimer-orphan-orphan-trimer-dimer or dimer-orphan-trimer-trimer-orphan-dimer. In short, it would result in one of the following possibilities:

- Bi-layers of both orphans or trimers - magnetically isolated by a layer of dimers;
- Magnetically isolated stack composed by four layers in the order: trimer-orphan-orphan-trimer or orphan-trimer-trimer-orphan. For illustration purposes, the latter is shown in Figure 5.2.

Figure 5.2: Four layers stack of triangular lattices as a possible magnetic emerging lattice. The blue layers are composed by orphan spins only, with $S = 3/2$, and the red layers are composed by magnetic trimers, that in low temperature are effective $S = 1/2$.

Such formation would not be detected by conventional X-ray diffraction, since it cannot distinguish the magnetic trimer, dimer and orphan spin. Only Resonant Magnetic X-ray diffraction or some technique that detects the magnetic moment of the Mn would measure such formation. This is one point that requires further investigation in order to discard or endorse such emerging lattices.

Additionally, other possibility is that, instead of the emerging lattices discussed above, the effective lattice formed by orphans and magnetic trimers is, in fact, not ordered, being a random lattice, as shown in Figure 5.2. This scenario favors the appearance of a spin glass state, which is known to emerge by the presence of disorder, and is not subjected to the symmetry restraints mentioned previously. The counting of fraction in this case would be the disordered counting defined in section 3.2.2.

Figure 5.3: Model of the proposed disordered emerging magnetic lattice at low temperature. Half of the M(2) sites are filled with Mn atoms (purple) and the other half by Ti atoms (blue), in a disordered way, that is statistically determined.

The greater difference in the experimental interpretation lies in the residual entropy analysis: the value of $2/3$ of residual entropy recovered at low temperatures suggests that some other ground state could exist at even lower temperatures, not being accessed by our experiments, which supports the spin glass scenario. On the other hand, the value of 91% of residual entropy recovered at low temperatures does not support this suggestion, and it more accurate when the symmetry of the unit cell is considered.

Therefore, considering the entropy, it is likely that the disorder in this case does not give origin to a spin glass ground state, but to a inhomogeneous spin liquid ground state.

These emerging magnetic lattices are not far from speculation right now. To further explore these possible emerging lattices, some theoretical effort must be done along with magnetic characterization, to study the magnetic lattice formed by the Mn in the material.

5.2 The Nature of the Dynamic Magnetic State

Theoretical explanations and predictions for the formation of a spin liquid state are part of a field still under development. As mentioned in the Introduction, the greatest challenge of this field of research is to reach a method to determine the presence of a spin liquid state unambiguously. Also, some difficulties lie in the explanation for the emergence of such state, for example, in identifying the kind of emerging magnetic lattice and its interactions responsible for the magnetic frustration, as explained in the previous section.

It is certain that in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ great magnetic frustration is present. This is clear from the fact that there is no sign of ordering for temperatures as low as 0.1 K in the magnetic susceptibility and specific heat and considering the characteristic interaction scales in the system, as discussed in chapter 3. We can infer that the frustration results from the magnetic orphan spins and trimers interacting in the emerging magnetic lattice, as discussed in the previous section, which is an interaction of order 10 K. This energy scale must not be mistaken by the interactions responsible for the magnetic trimers formation, which are of about 175 K and 100 K. Although these interactions introduce frustration, this is only a local frustration, acting only inside the structural trimers, while at low temperatures we are certainly probing a global frustration. In this regard, the frustration factor is at least of the order of 100.

Taking into account all experimental results presented and discussed in the previous chapters, we have enough evidence to assume that the most plausible state that the $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ achieves in the lowest temperatures is a gapless spin liquid.

The spin glass scenario could be one possible state for the low temperature spin dynamics. μSR data indicates dynamic magnetism down to $T = 0.019$ K with the relaxation rate λ going from $\approx 1.2 \mu\text{s}^{-1}$ for $T < 1$ K to $\approx 0.1 \mu\text{s}^{-1}$ for $T > 10$ K. A large jump in the relaxation rate like this one is reminiscent of spin glass state, but not exclusively. It also occurs for $\text{PbCuTe}_2\text{O}_6$ [50] or $\text{Tm}_3\text{Sb}_3\text{Zn}_2\text{O}_{14}$ [53], recently proposed spin liquid candidates. The λ jump for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ suggests a glass transition temperature (T_g) of about $T_g \approx 1 - 2$ K. But, as mentioned in chapter 3, from the AC susceptibility $\chi'(T)$ data, it is safe to assume that there is no sign of a spin glass state for temperatures as low as 1.8 K, ruling out the possibility of the formation of a spin glass in the crossover region. Certainly, $\chi'(T)$ measurements at lower temperatures are needed for a more conclusive statement.

Still concerning the μSR data, the lack of the characteristic recovery of 1/3 of the μ^+ polarization expected for glassy systems [47] in the ZF measurements at low temperature (Figure 4.2) favors the spin liquid state possibility.

The disorder of the spins in the system could be the origin for a spin glass state, but maybe it also could explain a spin liquid behavior. In short, the low temperature dynamic magnetic state in our system displays spin liquid behavior, although a spin glass state, induced by disorder, is also a strong candidate to interpret our results.

Given the considerations above, we are compelled to search in the literature for theoretical models that could describe the magnetic state that we have characterized.

One possible spin liquid model for this system would be a spin liquid with a spinon Fermi-surface. In this kind of spin liquid, the magnetic susceptibility saturates at low temperatures, which occurs for our system, as shown in Figure 3.1. However, for zero field, it is expected $C_{\text{mag}} \sim T^{2/3}$ [49, 54], which differs from the behaviour we observe in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$: $C_{\text{mag}} \approx T^{1.4-1.5}$ for $0.3 \text{ K} < T < 1 \text{ K}$, as discussed in the section 3.5.

Another possibility would be an $U(1)$ Dirac spin-liquid, which occurs in Kagome lattice with Heisenberg interaction [55, 56, 57]. For this kind of spin liquid system it is expected

$C_{\text{mag}} \sim T^2$ at zero fields, $C_{\text{mag}} \sim T$ at low fields and that C_{mag} should increase with the field, which we also do not observe. Furthermore, given our lattice geometry and symmetry, as well as the counting of orphan spins, magnetic dimers and trimers, it is unlikely that a Kagome lattice would be emerging, as observed in the previous section.

One spin liquid candidate that also presents similar impasses and is currently under debate is YbMgGaO_4 . In this system the emerging magnetic lattice is an triangular lattice formed by atoms of Yb^{3+} with $S = 1/2$ and with first and second neighbors antiferromagnetic interactions. One similarity is that the μSR results for YbMgGaO_4 are qualitatively similar to the result for $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ [49].

The observed spin liquid behavior in YbMgGaO_4 is not explained by the minimal theoretical models [12, 49, 58, 59]. It is possible that the presence of disorder in the system is responsible for the spin liquid state [60]. The disorder effects may have non-trivial consequences such as the formation of a ground state that does not present long range magnetic order [61, 62, 63]. Therefore we can not exclude the possibility of disorder in the formation of the spin liquid behavior in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$.

From the ordered counting applied to the experimental data, the magnetic entropy recovered in the magnetic specific heat corresponds only to $2/3$ of the expected entropy. That means that the dynamic magnetism state includes some residual entropy. This kind of behavior is also observed in other spin liquids candidates [64, 65]. One explanation for the remaining entropy is that the lowest temperatures that we achieved in our experiments are not enough to reach the true ground state, and that the state we observe is not the ground state, but a transition state, probably formed by an order achieved by the interactions in the emerging magnetic lattice presented in Figure 5.1.

5.3 Summary and Conclusion

Macroscopic and microscopic experiments were performed in the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. The main results can be thus summarized:

- No sign of magnetic order for temperatures as low as 0.1 K in the specific heat data and magnetic susceptibility;
- For temperatures in the region $0.2 \text{ K} < T < 1 \text{ K}$, the magnetic specific heat C_{mag} is proportional to $T^{1.4}$;
- The effective magnetic degrees of freedom are composed by orphan spins ($S = 3/2$) and trimers ($S = 1/2$);
- The remaining magnetic interaction in the low temperature region is of the order of 10 K, resulting in a frustration factor of about 100;

- The entropy recovered in the lowest temperature region corresponds to 66% or 91% of expected, depending on the counting of magnetic trimers, dimers and orphan spins.
- Macroscopic and microscopic measurements indicate the existence of a *crossover region* between 1.5 K and 10 K;
- μ SR regime below 1.5 K shows long time spin correlation;
- μ SR indicates the presence of dynamic magnetism down to $T = 19$ mK.

Taking into account all that was studied and discussed, the most likely scenario is an inhomogeneous gapless spin liquid ground state induced by disorder.

Another possible ground state is a spin glass with very low transition temperature (below 1.8 K), which would be under the influence of quantum fluctuations below the crossover region. To confirm or discard such possibility, AC susceptibility measurements at even lower temperature must be performed.

The proper characterization of the ground state requires further theoretical and experimental efforts. The next steps concerning the magnetic characterization of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ include the growth of single crystal samples for the use of other experimental techniques to probe its structure, as well as direct magnetic characterization methods, such as Resonant Inelastic X-ray Scattering (RIXS) and neutron based techniques.

Bibliography

- [1] J. Knolle and R. Moessner, arXiv preprint arXiv:1804.02037 (2018).
- [2] P. W. Anderson, Materials Research Bulletin **8**, 153 (1973).
- [3] C. Lacroix, P. Mendels, and F. Mila, eds., *Introduction to Frustrated Magnetism: Materials, Experiments, Theory*, Springer Series in Solid-State Sciences (Springer-Verlag, 2011).
- [4] J. E. Greedan, J. Mater. Chem. **11**, 37 (2001).
- [5] L. Balents, Nature **464**, 199 (2010).
- [6] S. T. Bramwell and M. J. P. Gingras, Science **294**, 1495 (2001).
- [7] C. Castelnovo, R. Moessner, and S. Sondhi, Annual Review of Condensed Matter Physics **3**, 35 (2012).
- [8] A. P. Ramirez, Annual Review of Materials Science **24**, 453 (1994).
- [9] X. Obradors, A. Labarta, A. Isalgué, J. Tejada, J. Rodriguez, and M. Pernet, Solid State Communications **65**, 189 (1988).
- [10] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, Rev. Mod. Phys. **82**, 53 (2010).
- [11] R. Coldea, D. A. Tennant, A. M. Tsvelik, and Z. Tylczynski, Phys. Rev. Lett. **86**, 1335 (2001).
- [12] J. A. Paddison, M. Daum, Z. Dun, G. Ehlers, Y. Liu, M. B. Stone, H. Zhou, and M. Mouri-gal, Nature Physics **13**, 117 (2017).
- [13] W. Liu, Z. Zhang, J. Ji, Y. Liu, J. Li, X. Wang, H. Lei, G. Chen, and Q. Zhang, Chinese Physics Letters **35**, 117501 (2018).
- [14] A. L. Chernyshev and M. E. Zhitomirsky, Phys. Rev. B **79**, 144416 (2009).
- [15] S. Yan, D. A. Huse, and S. R. White, Science **332**, 1173 (2011).
- [16] A. S. Wills, Canadian Journal of Physics , 1501 (2001).
- [17] J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, Phys. Rev. Lett. **98**, 107204 (2007).
- [18] Z. Hiroi, M. Hanawa, N. Kobayashi, M. Nohara, H. Takagi, Y. Kato, and M. Takigawa, Journal of the Physical Society of Japan **70**, 3377 (2001).

- [19] T. Yavors’kii, W. Apel, and H.-U. Everts, *Phys. Rev. B* **76**, 064430 (2007).
- [20] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato, and C. Baines, *Phys. Rev. Lett.* **98**, 077204 (2007).
- [21] C. Balz, B. Lake, J. Reuther, H. Luetkens, R. Schönemann, T. Herrmannsdörfer, Y. Singh, A. N. Islam, E. M. Wheeler, J. A. Rodriguez-Rivera, *et al.*, *Nature Physics* **12**, 942 (2016).
- [22] A. Kitaev, *Annals of Physics January Special Issue*, **321**, 2 (2006).
- [23] J. c. v. Chaloupka, G. Jackeli, and G. Khaliullin, *Phys. Rev. Lett.* **105**, 027204 (2010).
- [24] Y. Singh and P. Gegenwart, *Phys. Rev. B* **82**, 064412 (2010).
- [25] Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst, and P. Gegenwart, *Phys. Rev. Lett.* **108**, 127203 (2012).
- [26] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, *Phys. Rev. B* **90**, 041112 (2014).
- [27] P. Lampen-Kelley, L. Janssen, E. C. Andrade, S. Rachel, J.-Q. Yan, C. Balz, D. G. Mandrus, S. E. Nagler, and M. Vojta, *arXiv:1807.06192 [cond-mat]* (2018).
- [28] A. Banerjee, C. A. Bridges, J.-Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, *Nature Materials* **15**, 733 (2016).
- [29] A. Banerjee, J. Yan, J. Knolle, C. A. Bridges, M. B. Stone, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, R. Moessner, and S. E. Nagler, *Science* **356**, 1055 (2017).
- [30] G. M. Keith, C. A. Kirk, K. Sarma, N. M. Alford, E. J. Cussen, M. J. Rosseinsky, and D. C. Sinclair, *Chemistry of materials* **16**, 2007 (2004).
- [31] R. M. White, *Quantum Theory of Magnetism: Magnetic Properties of Materials*, 3rd ed., Springer Series in Solid-State Sciences (Springer-Verlag, 2007).
- [32] F. A. Garcia, U. F. Kaneko, E. Granado, J. Sichelschmidt, M. Hölzel, J. G. S. Duque, C. A. J. Nunes, R. P. Amaral, P. Marques-Ferreira, and R. Lora-Serrano, *Physical Review B* **91**, 224416 (2015).
- [33] L. Miranda, A. Feteira, D. C. Sinclair, K. Boulahya, M. Hernando, J. Ramírez, A. Varela, J. M. González-Calbet, and M. Parras, *Chemistry of materials* **21**, 1731 (2009).
- [34] J. Als-Nielsen and D. McMorrow, *Elements of Modern X-ray Physics, 2nd Edition* (John Wiley & Sons, 2011).
- [35] J.-L. Hodeau, V. Favre-Nicolin, S. Bos, H. Renevier, E. Lorenzo, and J.-F. Berar, *Chemical Reviews* **101**, 1843 (2001).
- [36] Y. Joly, S. D. Matteo, and O. Bunău, *The European Physical Journal Special Topics* **208**, 21 (2012).
- [37] A. M. G. Carvalho, D. H. C. Araújo, H. F. Canova, C. B. Rodella, D. H. Barrett, S. L. Cuffini, R. N. Costa, and R. S. Nunes, *Journal of Synchrotron Radiation* **23**, 1501 (2016).

- [38] J. Rodríguez-Carvajal, *Physica B: Condensed Matter* **192**, 55 (1993).
- [39] S. Blundell, *Magnetism in condensed matter* (Oxford University Press, Oxford, New York, 2003).
- [40] I. Wolfram Research, “Mathematica, Version 11.3,” (2018), champaign, IL.
- [41] M. Hortal, S. Vieira, and R. Villar, *Ferroelectrics* **54**, 313 (1984).
- [42] W. Proctor, R. G. Scurlock, and E. M. Wray, *Proceedings of the Physical Society* **90**, 697 (1967).
- [43] Y. Singh, Y. Tokiwa, J. Dong, and P. Gegenwart, *Phys. Rev. B* **88**, 220413 (2013).
- [44] S. J. Blundell, *Contemporary Physics* **40**, 175 (1999).
- [45] A. Suter and B. Wojek, *Physics Procedia* **30**, 69 (2012), 12th International Conference on Muon Spin Rotation, Relaxation and Resonance (μ SR2011).
- [46] A. Yaouanc and P. D. De Reotier, *Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter*, International Series of Monographs on Physics (Oxford University Press, Oxford, New York, 2011).
- [47] Y. J. Uemura, T. Yamazaki, D. R. Harshman, M. Senba, and E. J. Ansaldo, *Phys. Rev. B* **31**, 546 (1985).
- [48] Y. J. Uemura, A. Keren, K. Kojima, L. P. Le, G. M. Luke, W. D. Wu, Y. Ajiro, T. Asano, Y. Kuriyama, M. Mekata, H. Kikuchi, and K. Kakurai, *Phys. Rev. Lett.* **73**, 3306 (1994).
- [49] Y. Li, D. Adroja, P. K. Biswas, P. J. Baker, Q. Zhang, J. Liu, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, *Phys. Rev. Lett.* **117**, 097201 (2016).
- [50] P. Khuntia, F. Bert, P. Mendels, B. Koteswararao, A. V. Mahajan, M. Baenitz, F. C. Chou, C. Baines, A. Amato, and Y. Furukawa, *Phys. Rev. Lett.* **116**, 107203 (2016).
- [51] R. Kubo and T. Toyabe, “Magnetic resonance and relaxation,” (1967).
- [52] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, *Phys. Rev. B* **20**, 850 (1979).
- [53] Z.-F. Ding, Y.-X. Yang, J. Zhang, C. Tan, Z.-H. Zhu, G. Chen, and L. Shu, *Phys. Rev. B* **98**, 174404 (2018).
- [54] O. I. Motrunich, *Phys. Rev. B* **72**, 045105 (2005).
- [55] Y. Ran, M. Hermele, P. A. Lee, and X.-G. Wen, *Phys. Rev. Lett.* **98**, 117205 (2007).
- [56] S. Ryu, O. I. Motrunich, J. Alicea, and M. P. A. Fisher, *Phys. Rev. B* **75**, 184406 (2007).
- [57] Y.-C. He, M. P. Zaletel, M. Oshikawa, and F. Pollmann, *Phys. Rev. X* **7**, 031020 (2017).
- [58] Y. Li, H. Liao, Z. Zhang, S. Li, F. Jin, L. Ling, L. Zhang, Y. Zou, L. Pi, Z. Yang, *et al.*, *Scientific reports* **5**, 16419 (2015).
- [59] Y. Li, G. Chen, W. Tong, L. Pi, J. Liu, Z. Yang, X. Wang, and Q. Zhang, *Phys. Rev. Lett.* **115**, 167203 (2015).

- [60] Y. Li, D. Adroja, R. I. Bewley, D. Voneshen, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, Phys. Rev. Lett. **118**, 107202 (2017).
- [61] Z. Zhu, P. A. Maksimov, S. R. White, and A. L. Chernyshev, Phys. Rev. Lett. **119**, 157201 (2017).
- [62] E. C. Andrade, J. A. Hoyos, S. Rachel, and M. Vojta, Phys. Rev. Lett. **120**, 097204 (2018).
- [63] E. Parker and L. Balents, Phys. Rev. B **97**, 184413 (2018).
- [64] R. Kumar, P. Khuntia, D. Sheptyakov, P. G. Freeman, H. M. Rønnow, B. Koteswararao, M. Baenitz, M. Jeong, and A. V. Mahajan, Phys. Rev. B **92**, 180411 (2015).
- [65] R. Kumar, D. Sheptyakov, P. Khuntia, K. Rolfs, P. G. Freeman, H. M. Rønnow, T. Dey, M. Baenitz, and A. V. Mahajan, Phys. Rev. B **94**, 174410 (2016).

Annex

Scientific outputs related to this work

Poster presentation:

- Event: 28 RAU (Annual Users Meeting) of LNLS/CNPEM. Title: "Resonant X-Ray Diffraction of the spin liquid candidate $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ ".

Published paper:

- Physical Review B 99, 054412 (2019): it summarizes the work of this master's thesis. It can be found as an annex in the following pages.

"Dynamic magnetism in the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ ".

Authors: M.R. Cantarino, R.P. Amaral, R.S. Freitas, J.C.R. Araújo, R. Lora-Serrano, H. Luetkens, C. Baines, S. Bräuninger, V. Grinenko, R. Sarkar, H.H. Klauss, E. C. Andrade, F. A. Garcia.

Other scientific outputs

Published paper:

- Physical Review B 99, 035152 (2019). My contribution includes participating in experiments at the beamlines XAFS2 and XDS of the brazilian synchrotron light source (LNLS/CNPEM), and doing simulations of XANES and EXAFS spectra using the FEFF software.

"Hard X-ray spectroscopy of the itinerant magnets $R\text{Fe}_4\text{Sb}_{12}$ ($R = \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba}$)".

Authors: Bassim Mounssef Jr., Marli R. Cantarino, Eduardo M. Bittar, Tarsis M. Germano, Andreas Leithe-Jasper, Fernando A. Garcia.

Dynamic magnetism in the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$

M.R. Cantarino¹, R.P. Amaral², R.S. Freitas¹, J.C.R. Araújo², R. Lora-Serrano², H. Luetkens³, C. Baines³, S. Bräuninger⁴, V. Grinenko⁴, R. Sarkar⁴, H.H. Klauss⁴, E. C. Andrade⁵, F. A. Garcia¹

¹*IFUSP, Universidade de São Paulo, 05508-090, São Paulo-SP, Brazil*

²*Universidade Federal de Uberlândia, Instituto de Física, 38400-902, Uberlândia-MG, Brazil*

³*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*

⁴*Institute for Solid State and Material Physics, TU Dresden, D-01069 Dresden, Germany and*

⁵*Instituto de Física de São Carlos, Universidade de São Paulo, C.P. 369, São Carlos, SP, 13560-970, Brazil*

Magnetic frustration and disorder are key ingredients to prevent the onset of magnetic order. In the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, Mn^{4+} cations, with $S = 3/2$ spins, can either form highly correlated states of magnetic trimers or dimers or remain as weakly interacting orphan spins. At low temperature (T), the dimer response is negligible, and magnetism is dominated by the trimers and orphans. To explore the role of magnetic frustration, disorder and possibly of quantum fluctuations, the low- T magnetic properties of the remaining magnetic degrees of freedom of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ are investigated. Heat-capacity data and magnetic susceptibility display no evidence for a phase transition to a magnetically ordered phase but indicate the formation of a correlated spin state. The low-temperature spin dynamics of this state is then explored by μSR experiments. The zero field μ^+ relaxation rate data show no static magnetism down to $T = 19$ mK and longitudinal field experiments support as well that dynamic magnetism persists at low T . Our results are interpreted in terms of a spin glass state which stems from a disordered lattice of orphans spins and trimers. A spin liquid state in $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, however, is not excluded and is also discussed.

I. INTRODUCTION

Transition metal (M) oxides are forever the source of intriguing physics in the field of correlated electron systems, including a large number of complex magnetic systems [1]. Complexity emerges from the magnetic interaction between the spins at the M sites, which takes place by means of a superexchange interaction [2] that will usually drive the system to a magnetic ordered state [3]. In some materials, however, dimensionality, disorder, lattice geometry or the symmetry of the interactions may hinder the appearance of long range order [4–8]. In these cases, the system will remain in a dynamic magnetic state. This dynamic magnetic state may either be identified as a spin freezing phenomenon [9, 10] or, at sufficient low temperatures (T), the system may be driven by quantum fluctuations to some exotic ground state, such as a quantum spin liquid ground state. A spin liquid state is a disordered quantum magnetic state wherein the spins are entangled in a highly correlated and dynamic state of matter [11–13].

The first task to experimentally verify the formation of a spin liquid state is to provide evidence for the lack of phase transitions down to the lowest temperatures. It is paramount, as well, to present evidence that a collective spin state is formed at low- T , most striking by characterizing continuous magnetic excitations [14–16] or the spin relaxation rate regime. For the later purpose, muon spin relaxation (μSR) is a particular appropriate technique [17–20]. The task, however, cannot be settled based upon μSR measurements alone, since a dynamic magnetic state without strong quantum fluctuations (such as a spin glass) will also display an evolution of the relaxation regime [9, 21] which hold some similarity to what

is found for some spin liquid candidates [20, 22].

In the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$, $S = 3/2$ spins due to Mn^{4+} cations pair up to form magnetic dimers in a singlet state, coexisting with orphan spins and magnetic trimers [23]. The formation of dimers and trimers are dictated by large energy scales ($\approx 101 - 176$ K). The effective low- T degrees of freedom involve orphan spins and trimers, distributed in layers of triangular lattices, with competing antiferromagnetic exchange interactions. The distinct layers are well spaced, making the interactions mainly of intralayer character. As we shall discuss, this distribution of orphans and trimers implies a large magnetic frustration, with a lower bound for the frustration parameter (f) of about ≈ 75 .

In this paper, we show that this configuration paves the way for the existence of a dynamic magnetic state at low T in our system, comprised of correlated $S = 3/2$ (orphans) and effective $S = 1/2$ spins (trimers). We present and discuss low- T heat capacity and susceptibility data which show no sign of long-range order, but which indicate a highly correlated magnetic state. Subsequently, we explore the spin dynamics of our system by μSR , and it is shown that dynamic magnetism persists down to the lowest temperatures ($T = 0.019$ K) achieved in our experiments. Our results and analysis support that this dynamic magnetic state can be interpreted as a spin glass state. However, a spin liquid scenario is not excluded and is discussed as well.

II. METHODS

High quality polycrystalline samples were synthesized by the solid state reaction method as in Ref. [23]. Synchrotron X-ray diffraction experiments were carried out at the XRD1 beamline of the LNLS-CNPEM, Brazil [24]. Heat capacity measurements were performed to temperatures down to 0.1 K and magnetic fields up to 9 T, employing a Quantum Design PPMS, using a dilution refrigerator. DC and AC susceptibility ($\chi(T)$ and $\chi'(T)$) measurements were performed for temperatures down to 0.6 K employing a Quantum Design MPMS (1.8–300 K) and a Vibrating Sample Magnetometer (VSM) in a ^3He cryostat.

μSR measurements have been carried out at the πM3 beam line at the GPS and LTF spectrometers of the Swiss Muon Source at the Paul Scherrer Institute (PSI) in Villigen. The measurements were performed in the T interval $0.019 < T < 10$ K (LTF) and $1.5 < T < 200$ K (GPS) [25] in zero magnetic field (ZF) and in longitudinal applied magnetic fields (LF) with respect to the initial muon spin polarization up to 0.05 T. To improve the thermal contact, the samples in the experiments at the LTF spectrometer were glued on a Ag plate. This gives rise to a time and temperature independent background due to muons that stopped in the Ag plate. The μSR time spectra were analyzed using the free software package MUSRFIT [26]. DFT calculations of the electrostatic potential were performed to extract information about the muon local environment. We employed the all-electron full-potential linearized augmented-plane wave code Elk 4.3.6, which includes the Spacegroup package using Broyden mixing [27] and the Generalized Gradient Approximation functional [28].

III. RESULTS AND DISCUSSION

A. Structure, magnetism and heat capacity

The $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ structure is presented in Fig. 1(a) [23, 29, 30] (see Ref. [31] for further support from new resonant diffraction experiments). The structure possesses 3 transition metal sites, termed $M(1)$, $M(2)$ and $M(3)$. Mn cations are found at the $M(1)$ and $M(2)$ sites, inside the structural trimers. The $M(1)$ sites are occupied exclusively by Mn atoms whereas the occupation of the $M(2)$ sites is mixed.

All analysis so far [23, 29, 30] and our results [31] support that the $M(2)$ site is equally occupied by either Mn or Ti atoms. Therefore, the relative fraction of dimers, trimers and orphans are statistically determined as in Ref. [23]. It results that $1/8$ of the Mn are orphans, half pair up to form dimers and $3/8$ form trimers. The coupling of magnetic dimers and trimers are described by two strong exchange constants J_1 and J_2 (Fig. 1(b)), which were shown to be of comparable size [23].

Figure 1. (a) Structural model of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$ with a 12R-type perovskite structure (as in Ref. [23]). Barium (Ba(1) and Ba(2)), oxygen (O(1) and O(2)) and transition metal ($M(1)$, $M(2)$ and $M(3)$) sites are indicated. (b) Detail of the structural trimer indicating the J_1 and J_2 exchange constants. (c) Model of the proposed emerging magnetic lattice at low T . Half of the $M(2)$ sites are filled with Mn atoms (purple) and the other half by Ti atoms (blue), in a disordered way, that is statistically determined.

As a function of T , the dimer contribution to magnetism is exponentially suppressed and we can safely assume that at low- T the remaining magnetic degrees of freedom are due to orphan spins and magnetic trimers. Focusing on the plane formed by the $M(1)$ sites, one may propose the following emerging 2D structure for the magnetic lattice, represented in Fig. 1(c): layers of randomly distributed magnetic trimers and orphans and dimers in a triangular lattice (lattice constant $a = 5.69 \text{ \AA}$). The dimers, being non-magnetic at low T , act essentially to dilute the magnetic interactions in the system. Distinct layers of this magnetic lattice are in a AB stacking and interlayer interaction may be possible, however, consecutive layers are separated by $\approx 9.8 \text{ \AA}$ and this interaction is likely weak.

In panel (a) of Fig. 2 we present heat capacity measurements, C_p , as a function of T ($0.2 < T < 100 \text{ K}$) for distinct values of H . The data give no evidence for a phase transition down to $T = 0.2 \text{ K}$, presenting only a broad anomaly peaking at about 3 K for $H = 0$, that we shall interpret as a crossover to the dynamic magnetic state. Below and about $T \lesssim 0.2 \text{ K}$, the data present an upturn at low $-T$ that could be interpreted as the tail of a transition at further lower temperatures. This upturn,

however, is actually due to the Mn nuclear contribution to the heat capacity. This conclusion is supported by the data presented in the inset of the same figure, wherein we compare the $H = 0$ data with the Mn nuclear heat capacity as measured in experiments with MnNi [32]. It is shown that it scales well with our data and, therefore, it is safe to assert that no phase transition is observed down to $T \approx 0.1$ K.

In panel (b), $\chi(T)$ measurements are presented in the interval $0.6 < T < 330$ K. To describe the data in the range $T > 5.5$ K, which is above the crossover region, we refer to our model [31] including magnetic dimers and trimers plus orphan spins. The obtained parameters associated to dimers and trimers are $J_1 = 176(5)$ K and $J_2 = 0.59(5)J_1$. In this parameter range, the trimer ground state is formed by effective $S = 1/2$ spins, which, along with the $S = 3/2$ spins from the Mn^{4+} orphans, are the remaining magnetic degrees of freedom at low- T . In the inset, it can be observed a trend towards saturation which cannot be related to a simple Curie-Weiss behavior. It rather indicates the absence of free paramagnetic spins in the system and thus we conclude that the effective $S = 1/2$ spins and orphan spins are correlated at low- T .

To estimate the energy scale of the correlated state of trimers and orphans, we model the orphan-trimer subsystem by a Curie-Weiss susceptibility, with parameters θ_{eff} and C_{eff} , obtaining $\theta_{\text{eff}} = -7.5(5)$ K and $C_{\text{eff}} = 0.19(1)$ emu.K/mol (f.u.) [31]. The value of θ_{eff} supports the idea of a highly frustrated system, with a lower bound for the frustration parameter of $f \gtrsim 7.5/0.1 = 75$. Here, θ_{eff} is to be understood as a phenomenological constant which sets the energy scale of the interactions between the remaining magnetic degrees of freedom: orphan-orphan, orphan-trimer and trimer-trimer interactions. In the context of the discussion of Fig. 1(c), it reflects mainly the intralayer interactions of the diluted magnetic lattice. As for $C_{\text{eff}} = 0.19(1)$ emu.K/mol (f.u.), it compares relatively well with $C \approx 0.14$ emu.K/mol (f.u.) expected for 1/16 mols of Mn $S = 3/2$ plus effective $S = 1/2$ spins per formula unit of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. In Fig. 2(c), $\chi'(T)$ measurements ($1.8 < T < 300$ K) at a broad range of frequencies (ν) do not depend on ν even in the interval $1.8 - 3$ K, that is below the crossover region. Such dependency could be expected, for instance, in spin glass systems.

The nature of the dynamic magnetic state will manifest in the behavior of magnetic specific heat C_{mag} . Following the subtraction of the phonon contribution (C_{lattice} , [31]), C_{mag} is presented in panel (a) of Fig. 3 for H up to 9 T. Inspecting the broad anomalies, we observe that the peaks displace to higher temperatures (from $T \approx 3 - 7$ K) with increasing field. To characterize the magnetic excitations of the low- T phase, we focus on the low temperature region ($0.2 \leq T \leq 1.0$ K). It is adopted that $C_{\text{mag}}(T)$ will in general follow a power law in the low- T region and the data are fitted to the expression $C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)}$. The dashed lines

Figure 2. (a) Heat capacity (C_p) measurements as a function of T and applied field H . The inset shows the Mn nuclear contribution to the heat capacity. (b) DC Susceptibility [$\chi(T)$] measurements as a function of T ($0.6 \leq T \leq 330$ K). The inset shows $\chi(T)$ data for $T < 2$ K. The fitting (thick line) is discussed in Ref. [31]. (c) AC Susceptibility [$\chi'(T)$] measurements as a function of T ($1.8 \leq T \leq 300$ K) at distinct frequencies.

are representative ($H = 0$ T and $H = 9$ T) fittings. The resulting parameters, $\gamma(H)$ and $\alpha(H)$, are shown in Fig. 3(b). Within error bars, $\alpha(H)$ is nearly constant assuming a value of about $\approx 1.45(5)$, suggesting gapless excitations of this low- T dynamic magnetic phase. Moreover, C_{mag}/T do not diverge as $T \rightarrow 0$, meaning that our system is away from quantum criticality [33]. The value of $\gamma(H)$ decreases with increasing field from $\gamma \approx 0.45$ to $\gamma \approx 0.25$ J/mol(Mn)K $^\alpha$ at $H = 9$ T, indicating quenching of the magnetic entropy as a function of the field, albeit there are no free spins in the system at this temperature range. These values are relatively large when compared to spin liquid candidates [34].

The nature of the zero field C_{mag} , in particular, is key to estimate the total entropy recovered in the ground state and to reveal the total fraction of spins that are part of the proposed correlated state. In Fig. 3(c), we show the heat capacity data and the magnetic entropy [$\Delta S(T)$] for $H = 0$ in the interval $0.1 \leq T \leq 10$ K, within which the entropy contribution from excited states of the trimer is negligible. The total entropy recovered by the system amounts to $\approx 1.97(5)$ J/K.mol(Mn). This number must be compared with the entropy expected from the remaining magnetic degrees of freedom at low- T [31], that amounts to 1/8 mols of $S = 3/2$ and effective $S = 1/2$ spins per mol of Mn atoms. Thus, the total expected entropy is $R/8(\ln 4 + \ln 2) \approx 2.16$ J/K.mol(Mn). The experimental result is certainly larger than what is expected for the orphan spins only [≈ 1.44 J/K.mol(Mn)], further suggesting that the remaining magnetic degrees of freedom must include $S = 3/2$ and effective $S = 1/2$ spins. Moreover, the trimers cannot be in a simple paramagnetic state for such state would imply (i) sizable Schottky

Figure 3. (a) Magnetic specific heat, $C_{\text{mag}}(T)$, obtained after the subtraction of the lattice contribution. The dashed lines are representative fittings ($H = 0$ and $H = 9$ T) to $C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)}$. (b) Full set of field dependent parameters $\gamma(H)$ and $\alpha(H)$ obtained from this fitting. (c) Zero field magnetic specific heat data and the total magnetic entropy $\Delta S(T)$.

anomalies in the field dependent heat capacity measurements, and (ii) a Curie-like response in the magnetic susceptibility, both which are not observed [31]. Overall, if we consider the total entropy due to trimers and orphans in the system, we may assert that we recover a total of $\approx 90\%$ of the expected system entropy.

B. μ SR ZF and LF experiments

We now turn our attention to our μ SR experiments [18]. In Fig. 4(a)-(d) we present ZF μ SR data measured for temperatures down to $T = 0.019$ K. Down to the lowest temperatures, the spectra (Figs. 4(a)-(b)) can be described quite well by an exponential decay, and the data do not present the characteristic damped oscillations of a magnetic ordered phase [18]. Fig 4(a) shows the temperature interval for which the spectra change the most ($1.5 < T < 10$ K), characterizing a crossover behavior in this region. Fig 4(b) display the low temperature spectra, which can be almost described by a single fitting below $T < 1.5$ K. The theoretical curves represent the best fitting to a stretched exponential which describes the asymmetry function $A(t) = A_0 \exp -(\lambda t)^\beta + B$, where A_0 is the starting asymmetry, B describes the constant background mostly due to muons that did not stop in the sample and λ and β are, respectively the relaxation rate and the stretching exponent. The muon environment was investigated by means of DFT calculations. The result proposes that the muon is located close to the Oxygen between the two Barium sites [31].

The resulting fitting parameters λ and β are shown in Figs 4(c)-(d). For $T > 10$ K, λ is nearly temperature independent, as typical for simple paramagnets. In the T -region $1.5 < T < 10$ K, λ goes through a steep increase from $\approx 0.06 \mu\text{s}^{-1}$ up to a constant value $\approx 1.2 \mu\text{s}^{-1}$ for $T < 1.5$ K, characteristic of a crossover behavior. The β coefficient do also display a crossover behavior in this same T -region. Its value decreases from ≈ 1 at high T to a constant value close to 0.5 for $T < 1.5$ K. This value is well above 1/3 that would be expected for glassy dynamics of simple systems, indicating the absence of static local fields [9, 18]. It is noteworthy that the crossover region detected by the μ SR corresponds closely to the region where the broad peak is observed for the heat capacity measurements. Our data illustrate a good qualitative agreement between macroscopic and microscopic measurements.

We have as well performed LF measurements at $T = 0.1$ K and the results are presented in Fig 4(e). The data is compared with the expected results from the dynamical Kubo-Toyabe (DKT) theory. The change in the spectra as a function of field (from 0 to 0.05 T) is much less dramatic than the expected from the DKT theory. This is a compelling piece of evidence for dynamic magnetism at temperatures down to $T = 0.1$ K. Following Refs. [17, 19], the spin fluctuation rates for temperatures above and below the crossover can be estimated [31]. The results are $\nu_{T>10\text{ K}} = 7.4(1) \times 10^{10}$ Hz and $\nu_{T<1.5\text{ K}} = 3.7(6) \times 10^6$ Hz, suggesting, without symmetry breaking, the onset of long-time spin correlations in the system for $T < 1.5$ K.

C. The nature of the dynamic magnetic state

By direct inspection, the ZF spectra at low T in Fig.4(b) lack the characteristic recovery of 1/3 of the μ^+ polarization expected for glassy systems [9], thus we start discussing the possibility of a spin liquid state. The experimental results from heat capacity are compatible with a gapless spin liquid. Because the magnetic susceptibility saturates at low T , a strong candidate would be a spin liquid with a spinon Fermi-surface. However, for the latter, we expect $C_{\text{mag}} \sim T^{2/3}$ [19, 35] at zero field, unlike the $\approx T^{1.4-1.5}$ we observe. Another possibility would be an $U(1)$ Dirac spin-liquid [36–38]. Here, one expects $C_{\text{mag}} \sim T^2$ at zero fields and $C_{\text{mag}} \sim T$ at low-fields, and that C_{mag} should increase with the field, which we also do not observe.

A similar drawback is recently under debate in YbMgGaO_4 , where the observed spin liquid behavior is not captured by the minimal theoretical model [15, 19, 34, 39]. One possible scenario to understand the reported experimental behavior is to take into account the presence of disorder in the system [40], which may have non-trivial effects, even leading to the destruction of long-range magnetic order [41–43]. Since the μ SR results for YbMgGaO_4 are qualitatively similar to ours [19], disorder is likely a relevant parameter to understand the

Figure 4. (a) – (b) Representative ZF- μ SR spectra measured at the (a) crossover region and (b) in the low- T region. Thick lines are the fittings of the data to a stretched exponential. Temperature dependency of the (c) μ^+ spin relaxation rate, λ and (d) stretching exponent, β as a function of T . (e) LF experiment ($T = 0.1$ K) spectra and comparison with the DKT theory.

behavior of $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$.

In this line of thinking, the large jump in λ is a drawback to the interpretation in terms of a spin liquid state, since it is reminiscent of spin glass behavior [9, 17, 21, 44]. Furthermore, a spin glass state is favored by the presence of a disordered magnetic lattice of $S = 3/2$ and effective $S = 1/2$ spins as suggested by our structural analysis. However, large jumps of λ can be found as well for $\text{PbCuTe}_2\text{O}_6$ [20] or $\text{Tm}_3\text{Sb}_3\text{Zn}_2\text{O}_{14}$ [22], which are all recently proposed spin liquid candidates, presenting a characteristic large λ of about $\approx 1.0\mu\text{s}^{-1}$ at low- T , as in the present case. The steep increase in λ suggests a glass transition temperature (T_g) of about $T_g \approx 1 - 2$ K and this must be contrasted with the frequency independence of $\chi'(T)$, specially in the region 1.8–3 K. Certainly, $\chi'(T)$ measurements down to lower temperatures are needed for a more conclusive statement.

Based upon the heat capacity analysis, we can account for 90% of the total entropy of the system. This result almost exclude the possibility that the probed dynamic

magnetic state could relate to a crossover region to an ordered state at further lower temperature. In particular, ferrimagnetic order due to the antiferromagnetic coupling of the unlike $S = 3/2$ and $S = 1/2$ spins [45, 46] is not to be expected. The existence of residual entropy is compatible with a spin glass and the dynamic magnetism probed by the ZF spectra at 0.019 K could be due to the fraction of spins that are not frozen due a distribution of time scales in a spin glass. However, residual entropy is also observed in spin liquid candidates [47, 48]. In short, the low- T dynamic magnetic state in our system displays spin liquid behavior, although a spin glass state, induced by the disordered lattice of orphans and trimers [41–43], is a strong candidate to interpret our results.

IV. SUMMARY AND CONCLUSIONS

We have performed macroscopic and microscopic experiments in the disordered hexagonal double perovskite $\text{BaTi}_{1/2}\text{Mn}_{1/2}\text{O}_3$. This complex material displays a rich magnetic behavior with the physics at high temperatures dominated by the presence of trimers, dimers, and orphan spins [23]. At lower temperatures, the effective magnetic degrees of freedom, composed by orphan spins and trimers, are found to be correlated but no phase transition is detected down to $T = 0.1$ K, despite the effective exchange couplings being of the order of 10 K. μ SR measurements then show substantial evidence for dynamic magnetism down to $T = 0.019$ K, the nature of which was discussed in terms of a spin liquid and a spin glass scenario. The proper characterization of this state requires further theoretical and experimental efforts.

ACKNOWLEDGMENTS

MRC acknowledges CNPq grant No.131117/2017-3 for financial support. The authors acknowledge CNPEM-LNLS for the concession of beam time (proposal No. 20160245). The XRD1 beamline staff is acknowledged for the assistance during the experiments. RSF acknowledges FAPESP grant No.2015/16191-5 and CNPq grant No.306614/2015-4. RLS acknowledges FAPEMIG-MG (APQ-02256-12) and CAPES Foundation (Brazil) for grant EST-SENIOR-88881.119768/2016-01. Author VG is supported by GR 4667. RS and HHK are partially supported by DFG SFB 1143 for the project C02. ECA acknowledges FAPESP Grant No. 2013/00681-8 and CNPq Grant No. 302065/2016-4.

[1] E. Dagotto, *Science* **309**, 257 (2005).
 [2] J. B. Goodenough, *Magnetism And The Chemical Bond* (Wiley, New York, 1963).

[3] R. M. White, *Quantum theory of magnetism magnetic properties of materials* (Springer, Berlin, 2007).
 [4] P. W. Anderson, *Mater. Res. Bull.* **8**, 153 (1973).

- [5] N. Read and S. Sachdev, *Phys. Rev. Lett.* **62**, 1694 (1989).
- [6] A. Kitaev, *Annals of Physics January Special Issue*, **321**, 2 (2006).
- [7] J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, *Phys. Rev. Lett.* **98**, 107204 (2007).
- [8] M. Mourigal, M. Enderle, A. Klöpperpieper, J.-S. Caux, A. Stunault, and H. M. Rønnow, *Nature Phys.* **9**, 435 (2013).
- [9] Y. Uemura, T. Yamazaki, D. Harshman, M. Senba, and E. Ansaldo, *Physical Review B* **31**, 546 (1985).
- [10] R. Moessner and A. P. Ramirez, *Physics Today* **59**, 24 (2006).
- [11] L. Balents, *Nature* **464**, 199 (2010).
- [12] L. Savary and L. Balents, *Rep. Prog. Phys.* **80**, 016502 (2017).
- [13] Y. Zhou, K. Kanoda, and T.-K. Ng, *Reviews of Modern Physics* **89**, 025003 (2017).
- [14] T.-H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, and Y. S. Lee, *Nature* **492**, 406 (2012).
- [15] J. A. M. Paddison, M. Daum, Z. Dun, G. Ehlers, Y. Liu, M. B. Stone, H. Zhou, and M. Mourigal, *Nature Physics* **13**, 117 (2017).
- [16] C. Balz, B. Lake, J. Reuther, H. Luetkens, R. Schönmann, T. Herrmannsdörfer, Y. Singh, A. T. M. Nazmul Islam, E. M. Wheeler, J. A. Rodriguez-Rivera, T. Guidi, G. G. Simeoni, C. Baines, and H. Ryll, *Nature Physics* **12**, 942 (2016).
- [17] Y. J. Uemura, A. Keren, K. Kojima, L. P. Le, G. M. Luke, W. D. Wu, Y. Ajiro, T. Asano, Y. Kuriyama, M. Mekata, H. Kikuchi, and K. Kakurai, *Physical Review Letters* **73**, 3306 (1994).
- [18] S. J. Blundell, *Contemporary Physics* **40**, 175 (1999).
- [19] Y. Li, D. Adroja, P. K. Biswas, P. J. Baker, Q. Zhang, J. Liu, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, *Physical Review Letters* **117**, 097201 (2016).
- [20] P. Khuntia, F. Bert, P. Mendels, B. Koteswararao, A. V. Mahajan, M. Baenitz, F. C. Chou, C. Baines, A. Amato, and Y. Furukawa, *Physical Review Letters* **116**, 107203 (2016).
- [21] G. T. Tran, P.-H. T. Nguyen, C. J. Bloed, M. E. Evans, J. A. Anczarski, W. P. Martin, J. Toro, D. V. Papakostas, J. Beare, M. N. Wilson, J. E. Greedan, G. M. Luke, T. Gredig, J. P. Carlo, and S. Derakhshan, *Physical Review B* **98**, 184401 (2018).
- [22] Z.-F. Ding, Y.-X. Yang, J. Zhang, C. Tan, Z.-H. Zhu, G. Chen, and L. Shu, *Physical Review B* **98**, 174404 (2018).
- [23] F. A. Garcia, U. F. Kaneko, E. Granado, J. Sichelschmidt, M. Hölzel, J. G. S. Duque, C. A. J. Nunes, R. P. Amaral, P. Marques-Ferreira, and R. Lora-Serrano, *Physical Review B* **91**, 224416 (2015).
- [24] A. M. G. Carvalho, D. H. C. Araújo, H. F. Canova, C. B. Rodella, D. H. Barrett, S. L. Cuffini, R. N. Costa, and R. S. Nunes, *Journal of Synchrotron Radiation* **23**, 1501 (2016).
- [25] A. Amato, H. Luetkens, K. Sedlak, A. Stoykov, R. Scheuermann, M. Elender, A. Raselli, and D. Graf, *Review of Scientific Instruments* **88**, 093301 (2017).
- [26] A. Suter and B. M. Wojek, *Physics Procedia 12th International Conference on Muon Spin Rotation, Relaxation and Resonance (μ SR2011)*, **30**, 69 (2012).
- [27] G. P. Srivastava, *Journal of Physics A: Mathematical and General* **17**, L317 (1984).
- [28] J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- [29] G. M. Keith, C. A. Kirk, K. Sarma, N. M. Alford, E. J. Cussen, M. J. Rosseinsky, and D. C. Sinclair, *Chemistry of Materials* **16**, 2007 (2004).
- [30] L. Miranda, A. Feteira, D. C. Sinclair, K. Boulahya, M. Hernando, J. Ramirez, A. Varela, J. M. Gonzalez-Calbet, and M. Parras, *Chemistry of Materials* **21**, 1731 (2009).
- [31] M. R. Cantarino, R. P. Amaral, R. S. Freitas, J. C. R. Araújo, R. Lora-Serrano, H. Luetkens, C. Baines, S. Bräuning, V. Grinenko, R. Sarkar, H. H. Klauss, E. C. Andrade, and F. A. Garcia, *Supplemental Material* (2018).
- [32] W. Proctor, R. G. Scurlock, and E. M. Wray, *Proceedings of the Physical Society* **90**, 697 (1967).
- [33] Y. Singh, Y. Tokiwa, J. Dong, and P. Gegenwart, *Physical Review B* **88**, 220413 (2013).
- [34] Y. Li, H. Liao, Z. Zhang, S. Li, F. Jin, L. Ling, L. Zhang, Y. Zou, L. Pi, Z. Yang, J. Wang, Z. Wu, and Q. Zhang, *Scientific Reports* **5**, 16419 (2015).
- [35] O. I. Motrunich, *Phys. Rev. B* **72**, 045105 (2005).
- [36] Y. Ran, M. Hermele, P. A. Lee, and X.-G. Wen, *Phys. Rev. Lett.* **98**, 117205 (2007).
- [37] S. Ryu, O. I. Motrunich, J. Alicea, and M. P. A. Fisher, *Phys. Rev. B* **75**, 184406 (2007).
- [38] Y.-C. He, M. P. Zaletel, M. Oshikawa, and F. Pollmann, *Phys. Rev. X* **7**, 031020 (2017).
- [39] Y. Li, G. Chen, W. Tong, L. Pi, J. Liu, Z. Yang, X. Wang, and Q. Zhang, *Physical Review Letters* **115**, 167203 (2015).
- [40] Y. Li, D. Adroja, R. I. Bewley, D. Voneshen, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, *Physical Review Letters* **118**, 107202 (2017).
- [41] Z. Zhu, P. A. Maksimov, S. R. White, and A. L. Chernyshev, *Phys. Rev. Lett.* **119**, 157201 (2017).
- [42] E. C. Andrade, J. A. Hoyos, S. Rachel, and M. Vojta, *Phys. Rev. Lett.* **120**, 097204 (2018).
- [43] E. Parker and L. Balents, *Phys. Rev. B* **97**, 184413 (2018).
- [44] A. Keren, P. Mendels, I. A. Campbell, and J. Lord, *Physical Review Letters* **77**, 1386 (1996).
- [45] E. Lieb and D. Mattis, *J. Math. Phys.* **3**, 749 (1962).
- [46] Y. Iqbal, T. Müller, P. Ghosh, M. J. P. Gingras, H. O. Jeschke, S. Rachel, J. Reuther, and R. Thomale, *Phys. Rev. X* **9**, 011005 (2019).
- [47] R. Kumar, D. Sheptyakov, P. Khuntia, K. Rolfs, P. G. Freeman, H. M. Rønnow, T. Dey, M. Baenitz, and A. V. Mahajan, *Physical Review B* **94**, 174410 (2016).
- [48] R. Kumar, P. Khuntia, D. Sheptyakov, P. G. Freeman, H. M. Rønnow, B. Koteswararao, M. Baenitz, M. Jeong, and A. V. Mahajan, *Physical Review B* **92**, 180411 (2015).