Spin excitations used to uncover the nature of the magnetically ordered ground state of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$

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(Dated: January 7, 2015)

We have used time-of-flight inelastic neutron scattering to measure the spin wave spectrum of the canonical half-doped manganite Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ in its magnetic and orbitally ordered phase. Comparison of the data, which cover multiple Brillouin zones and the entire energy range of the excitations, with several different models shows that only the CE-type ordered state provides an adequate description of the magnetic ground state, provided interactions beyond nearest neighbor are included. We are able to rule out a ground state in which there exist pairs of dimerized spins which interact only with their nearest neighbors. The Zener polaron ground state, which comprises strongly bound magnetic dimers, can be ruled out on the basis of gross features of the observed spin wave spectrum. A model with weaker dimerization reproduces the observed dispersion but can be ruled out on the basis of subtle discrepancies between the calculated and observed structure factors at certain positions in reciprocal space. Adding further neighbor interactions results in almost no dimerization, i.e. interpolating back to the CE model. These results are consistent with theoretical analysis of the degenerate double exchange model for half-doping.

I. INTRODUCTION

A characteristic of materials exhibiting strong electronic correlations is a delicate balance between multiple competing phases which can often be tuned with relatively modest changes in external parameters such as temperature, magnetic field, pressure or chemical doping. Preeminence amongst strongly correlated electron systems are transition metal oxides, which display phenomena as diverse as superconductivity, orbital order, and complex magnetic order. Most families of transition metal oxides have been studied extensively, and manganites are no exception.

Interest in the manganites in recent times has broadly centered on two phenomena – colossal magnetoresistance (CMR) and multiferroicity. CMR manganites are in many ways typical of strongly correlated electron systems, in that they exist at the cusp of several competing phases. For the particular case of (nearly) cubic R$_{1-x}$A$_x$MnO$_3$(where R is a rare-earth or La, and A is Ca, Sr, Ba, or Pb) and its layered analogs (R,A)$_2$Mn$_2$O$_4$ and (R,A)$_3$Mn$_2$O$_7$ such phases include charge-ordered, antiferromagnetic, ferromagnetic metal, and ferromagnetic insulator. In these perovskite manganites each Mn ion has three electrons in the t$_{2g}$ d-orbitals, and a fraction (1 – x) have one in the higher energy e$_g$ orbitals, whose spins are aligned parallel to the local t$_{2g}$ moment by strong intrasite exchange. The essential physics is a competition between delocalization of the e$_g$ electrons, favoring a homogeneous, fully spin polarized, ferromagnetic metal via double exchange, and localization due to lattice distortions trapping the e$_g$ electrons to form polarons. For x ∼ 0.3 the materials are typically ferromagnetic metals, with a sea of polarons in the insulating paramagnetic phase. The most marked CMR effects typically occur for those materials in which the polarons order in the half doped state, x ∼ 0.5, to give a charge and orbitally ordered insulating state for T < T$_{CO}$. The charge-ordering temperature. In the case of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$(PCMO) T$_{CO}$ = 260 K and the transition from a paramagnetic to antiferromagnetic phase occurs at T$_N$ = 180 K.

Despite its relevance to the defining properties of the CMR manganites, the nature of the charge-ordered state is far from well-understood. The picture widely assumed is of CE-type charge and magnetic ordering, illustrated in Fig. 1(a), first proposed by Goodenough. In a plane of the pseudocubic lattice, half the Mn ions are Mn$^{3+}$ (hence spin 3/2) and half are Mn$^{4+}$ (spin 2); the ions are coupled ferromagnetically along zig-zag chains, with antiferromagnetic (AFM) inter-chain coupling. Along the direction connecting nearest neighbor Mn positions the sites are occupied by alternating Mn$^{3+}$ and Mn$^{4+}$ ions, with the lobes of the d$_{3z^2-r^2}$ orbitals on the Mn$^{3+}$ sites themselves alternating between lying parallel and perpendicular to this direction. These planes are then stacked antiferromagnetically.

However, there are some puzzling experimental problems with this simple picture in various half-doped manganites, including La$_{0.5}$Sr$_{1.5}$MnO$_4$, Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. Bond valence sums applied to the Mn
ions typically reveal Mn valences of approximately 3.4+ and 3.6+ rather than the expected 3+ and 4+ at the two sites.\textsuperscript{4,12} X-ray resonant scattering at the Mn K-edge also suggests that the valences differ by the same amount.\textsuperscript{4,12} An alternative model that has been proposed is one in which adjacent Mn\textsuperscript{3+} and Mn\textsuperscript{4+} ions pair up via delocalization of the lone $e_g$ electron to produce a single strongly bound unit with spin $7/2$ known as a Zener polaron (ZP). They form a herringbone pattern, as shown in Fig. 1(b), with AFM coupling between parallel units, and FM coupling between perpendicular units. In Fig. 1(b) we show the $\phi = \pi/2$ arrangement of spins in the ZP model, where the spins in adjacent dimers along the $[1,0]$-axis are rotated by $\pi/2$, and in adjacent dimers along the $[0,1]$-axis are antiparallel. The same magnetic ordering scheme as shown in the CE model can be achieved in the ZP model with $\phi = 0$. The idea of the ZP emerged from a key single crystal neutron diffraction experiment on Pr\textsubscript{0.6}Ca\textsubscript{0.4}MnO\textsubscript{3} performed at a temperature below $T_{CO}$ in which the orientation of the elongated MnO\textsubscript{6} octahedra and off-center position of the two inequivalent Mn sites in the refinement suggest the formation of Mn–Mn pairs. The concept of Zener polarons has received theoretical support from various \textit{ab initio} calculations\textsuperscript{16,17} and additional experimental support from electron microscopy and diffraction measurements.\textsuperscript{18} However the idea remains very controversial.\textsuperscript{19–20}

Trying to distinguish between the charge ordered (CO)
CE and ZP models by diffraction is very subtle, which in part accounts for the controversy. However, in principle they can be distinguished from measurements of the spin wave dispersion relations. Figure 2 shows theoretical spin wave dispersion relations for the CE model (dashed line) and ZP model (solid line). At low energies the dispersion relations near the zone center are qualitatively very similar. The main difference, however, is the absence of the higher branches for the ZP model in the limiting case of strong intra-dimer exchange, because the binding of spins in pairs halves the number of spin wave modes (see Section IV. Discussion). In previous neutron inelastic scattering measurements of half-doped manganites these higher branches were not explored, largely due to the kinematic constraints of the triple-axis spectrometers on which the measurements were performed. Instead the authors of these studies favor the CE model (including second neighbor exchange, $J_{F2}$) over the ZP model because the dispersion perpendicular to the 1-dimensional zig-zag spin chains is much softer than that parallel to the chains, implying a weak antiferromagnetic inter-chain interaction. In contrast, they argue that of the nearest-neighbor inter-dimer exchange interactions in the ZP model, only that along the AF stacking direction results in significant dispersion because the other two (labeled by $J_{FU}$ within a chain and $J_{FD}$ between chains in Fig. 1(b)) are frustrated, resulting in weak or no dispersion perpendicular to the AF stacking direction. However, while this may be the case for the $\phi = \pi/2$ magnetic structure on the basis of symmetry, in the case when $\phi = 0$ there is no such a priori reason to be confident that $J_{FU}$ and $J_{FD}$ are similar.

In a recent time-of-flight (ToF) neutron spectroscopy study of the bilayer manganite Pr$_{(Ca_0.9Sr_{0.1})_2Mn_2O_7}$ (PCSMO) the higher branches of the dispersion which are present in the CE model but not in the ZP model were measured. This enabled the authors to show that the CE model clearly provides the best description of the ground state in this material. Furthermore, the observed dispersion required both second neighbor interactions $J_{F2}$ and $J_{F3}$ along the FM zig-zags, which was ascribed to indicating some itinerant electron character. The authors also proposed an alternative model which is a variation on the ZP model, shown in Fig. 1(c), in which the FM exchange between the (notional) Mn$^{4+}$ and Mn$^{4+}$ sites along a zig-zag are alternately stronger and weaker, that is, the Mn ions form weakly bound dimers. This model interpolates continuously from the CE model to the limiting ZP model for $\phi = 0$ as the intra-dimer and inter-dimer exchange constants vary from equality to the intra-dimer exchange overwhelming the inter-dimer exchange. The other couplings are antiferromagnetic between adjacent parallel and perpendicular dimers in different zig-zag chains, and ferromagnetic between perpendicular dimers in the same zig-zag chain. In PCSMO the differences between the dimer model and the CE model could be resolved in favor of the latter by inspecting maps of the intensity $S(Q, \omega)$ at a particular key energy, namely the top of the lower band of excitations.

In this paper we present an investigation of the spin excitation spectrum of Pr$_{0.5}Ca_{0.5}MnO_3$. This material was chosen since it is perhaps the canonical example of a CE-type half-doped manganite. Furthermore, the whole debate surrounding whether the CE or ZP model is an appropriate description of the ground state arose because of the pioneering work of Daoud-Aladine et al. on PCMO close to half-doping. We also wished to determine whether the conclusions of Johnstone et al. were specific to the two-dimensional bilayer example of a half-doped manganite, or are in fact more general. We compare our ToF inelastic neutron scattering measurements qualitatively and quantitatively to each of the CE, dimer and ZP models. We consider in detail the dispersion relations and dynamical structure factor, $S(Q, \omega)$, elucidating the specific features in the data that allow us to distinguish between the models. Despite the complication of six-fold twinning, we are able to show that the CE model provides the best description of our data.

II. EXPERIMENTAL METHODS

The ToF neutron scattering measurements were performed on the ARCS ToF chopper spectrometer at the Spallation Neutron Source, Oak Ridge National Laboratory. Data were collected with incident neutron energies ($E_i$) of 35, 70, and 140 meV, with the instru-
ment’s corresponding Fermi chopper frequencies chosen in order to give energy resolution \( \approx 0.05E_i \) (full-width half-maximum) at the elastic line. The sample used for these measurements comprised a single crystal of mass 1.57 g, grown as described previously. It was mounted in an aluminium can containing helium exchange gas. The can was then mounted on the cold finger of a closed-cycle refrigerator (CCR) and cooled to 5.5 K, at which temperature all measurements were performed. The sample was mounted with the \( a- \) and \( c- \) axes horizontal. For the data collected with \( E_i = 35 \) meV and \( E_i = 140 \) meV the sample was held in a single orientation, with the \( c- \) axis of the sample parallel to the incident neutron beam. The data in these configurations were collected for 4 hours and 29 hours respectively. We hereafter refer to measurements taken in this configuration as ‘single-shot’ datasets.

For the data collected with \( E_i = 70 \) meV, we performed a single-shot measurement with the \( c- \) axis of the sample parallel to the incident neutron beam, in which configuration we collected data for 14 hours. In addition we performed a measurement in which the sample \( c- \) axis was rotated about the vertical axis from parallel to perpendicular to the incident neutron beam, in 0.5° steps, with spectra recorded for \( \sim 1 \) hour at each orientation. The spectra at each orientation were then combined into a single large dataset using the HORACE software, allowing us to make a broad survey of the cross-section in the full 4-dimensional reciprocal space. We hereafter refer to measurements taken using this method as ‘multi-angle’ datasets. Such a broad survey is crucial for a complete understanding of this material since, unlike bilayer PC-SMO for example, the magnetic interactions have appreciable strength in all three dimensions. In a time-of-flight measurement of this nature energy transfer is coupled to the component of the wavevector \( Q \) parallel to the incident neutron wavevector \( k_i \). Only by performing measurements in multiple orientations (or alternatively with multiple incident energies) can one decouple \( Q \) and energy\(^{22}\). To illustrate this, we show in Fig. 3 the ARCS spectrometer’s detector coverage of reciprocal space for a single-shot run (\( c- \) axis parallel to the incident neutron beam) and for a 90° angle scan with \( E_i = 70 \) meV.

We have chosen to index reciprocal space according to space group \( Pbnm \)\(^{22}\). In this convention, the zig-zag chains propagate along the \((1,0,0)\)-direction, as shown in Fig. 1(a). This crystal structure is related to the cubic perovskite system, which has lattice parameter \( a_p = 3.85 \)Å, by \( a \approx b \approx \sqrt{2}a_p, c \approx 2a_p \). In PCMO we expect sixfold twinning of the crystal that is described by a systematic permutation of the principal axes of the pseudocubic lattice. We therefore expect magnetic Bragg peaks in the \( Pbnm \) convention with wavevectors \( k_1 = (1/2,0,L) \) and \( k_2 = (1/2,-1/2,L) \), and structural peaks with wavevector \( q = (0,1/2,L) \), where \( L \) is an integer, arising as a result of a Jahn-Teller distortion of the Mn-O octahedra and orbital ordering\(^{24}\). In order to demonstrate the effect of the twinning we show in Fig. 4 a series of planes with \( L = 0, 0.5 \) and 1 respectively. Of particular importance in diffraction experiments are the peaks arising from the magnetic order with wavevector \( k_2 \), since even with the six-fold twinning these peaks can be uniquely identified, whereas the \( k_1 \) and \( q \) peaks from different twins overlap. In analysis of INS data in which all of the twins are accounted for, this is less of an issue. In addition, we expect to observe crystal electric field transitions originating from the Pr ions. Experiments on \( \text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \) (ref. 28) show that there are transitions with energies 12.8 meV and 15.35 meV. We did not observe strong transitions (compared to the other sources of magnetic scattering) at these energies, however.

III. RESULTS

Figure 4 shows an overview of the dispersion from measurements with all three incident energies used. The
essential features shown here are that the dispersion is highly structured over the full energy range, but most importantly there are two branches to the dispersion with an energy gap between them. Qualitatively, we estimate the two branches to cover energies in the range $0 \lesssim E \lesssim 37$ meV and $42 \lesssim E \lesssim 75$ meV. The data shown in panels (a) - (c) are taken from single-shot datasets, so the component of $Q$ parallel to the incident neutron beam, $(0, 0, L)$, varies as a function of energy. This makes qualitative statements difficult to make, other than the obvious presence of two branches of spin waves, but the value of $L$ is known for each energy so these data can be used collectively to constrain the parameters of different spin wave models. In panel (d) we show data from the multi-angle dataset, so the value of $L$ is the same for all of the data presented. This serves to illustrate that the gap observed between the lower and upper branches of the spin wave dispersion is not an artefact of the way in which a gapless dispersion might project on to the curved $(Q, E)$ hypersurface of measured reciprocal space coordinates from a single-shot run.

To follow the evolution of the spin waves with energy, we show in Fig. 5 a series of intensity maps at fixed energy from single-shot runs, together with simulations using the CE model with the best fit parameters obtained in the next section. Because the value of $L$ changes with incident energy and energy transfer for a given $Q$ coordinate in these plots, we are mapping the $L$ dispersion as well as the in-plane dispersion. The first four panels $(a)$ to $(d))$ therefore show a spin wave which disperses from $(1, 1)$, with the fourth panel, $(d)$, showing the top of the lower branch of the spin waves. Panels $(e)$ and $(f)$ show the upper branch of spin waves, with the dispersion converging on $(1, 0)$ as the band maximum at $\sim 75$ meV is approached. This part of the spectrum can be understood, with reference in addition to the periodicity evident in Fig. 5c, as arising from dominant FM exchange between nearest neighbour Mn ions along the zig-zags.

### IV. DISCUSSION

The so-called degenerate double exchange model (DDEX$^{29,30}$, which is a more general version of double exchange, would be an appropriate starting point for analyzing our data. This model allows for different occupations of the two-fold degeneracy of the $e_g$ orbitals on a lattice of Mn sites, finite Hund’s coupling between the $e_g$ and $t_{2g}$ orbitals and superexchange between the core moments of the Mn ions. However, calculation of the excitation spectra within such a framework is, though possible, extremely difficult, so in the absence of such calculations, we therefore decided to use an effective Heisenberg Hamiltonian to model our data. Appropriate choice of exchange interactions yields the CE magnetic ground state or the ZP magnetic ground state with $\phi = 0$ or $\phi = \pi/2$.

To analyze the data quantitatively we calculated the dispersion relations and dynamical structure factors for the Heisenberg Hamiltonian $\mathcal{H} = -\sum_{<ij>} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, using linear spin wave theory for each of the CE, ZP and dimer models illustrated in Fig. 1(a-d), and fitted the calculated $S(Q, \omega)$, averaged with equal weight from each twin, to the data by least-squares refining the exchange constants $J_{ij}$. In the first part of the fitting procedure we obtained initial estimates for the various parameters by examination of the spectral features detailed below. We then fitted data from all single-shot and multi-angle runs simultaneously. The data that we fitted were all either one-dimensional cuts or two-dimensional slices taken at constant energy, so that the energy-dependent resolution of the spectrometer could be accounted for by using a fixed gaussian broadening of the calculated intensity, the width of which was chosen to match the resolution at each energy. Twenty eight one-dimensional cuts and
twelve two-dimensional slices were used in the fitting process, with the fit being performed simultaneously on all of them to determine a single set of best-fit parameters. The robustness of the fit parameters obtained was checked by using numerous different sets of starting values, to confirm that the fit always converged on the same result.

A. CE model

We start with the CE model. As has already been noted, the dominant exchange is the nearest-neighbor interaction $J_{F1}$ linking adjacent Mn ions along the zigzag chains. Examination of Fig. 5(c) shows that the maximum of the dispersion, which has the periodicity of a ferromagnet, is $\sim 75\text{ meV}$, and thus the strongest constraint on the size of $J_{F1}$ comes from fitting this part of the dispersion. We determined from our best fit that $J_{F1} = 9.01 \pm 0.02\text{ meV}$. This value is comparable to that measured in PCSMO $(11.39 \pm 0.05\text{ meV})$23, La$_{0.5}$Sr$_{1.5}$MnO$_4$ (9.98 meV)$^{23}$, the AFM CO phases of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (6.76 meV)$^{23}$, and a little larger than the typical values for the FM double exchange in metallic FM manganites$^{31,32}$. In other words, it is consistent with its origin being due to double exchange.

At much lower energies ($\sim 10\text{ meV}$) there is a branch of the dispersion with double this periodicity which arises from the antiferromagnetic coupling between zigzag chains, $J_A$. Variations in this parameter have negligibly small effects on features of the dispersion above $\sim 10\text{ meV}$, so in practice it can be determined from fits to the $E_i = 35\text{ meV}$ dataset alone, where the background arising from the tails of the elastic line at these low energies is minimized. The best fit yielded a value of $J_A = -0.45 \pm 0.01\text{ meV}$.

The existence of a gap in the dispersion at $(1/2,0)$ (Fig. 5(d)) immediately implies a halving of the periodicity in real space along the zig-zags. In the framework of an effective Heisenberg Hamiltonian this implies one or both of the second neighbor interactions $J_{F2}$ and $J_{F3}$. The position in energy and size of the gap between the lower and upper spin wave branches, shown schematically in Fig. 2 is entirely dependent on the next-nearest-neighbor terms $J_{F2}$ and $J_{F3}$. In order to reproduce the gross features observed these two parameters must have different values, and we find that in fact they must have opposite signs, as was similarly concluded for PCSMO$^{44}$. The size and position of the gap can be reproduced identically by exchanging the signs of $J_{F2}$ and $J_{F3}$, that is, with $J_{F2} < 0$ < $J_{F3}$ or $J_{F2} > 0$ > $J_{F3}$. However the details of the structure factor around the gap can distinguish between these two scenarios, specifically spectral weight is swapped between two relatively flat branches of the dispersion that lie at the top of the lower set of spin wave branches and the bottom of the upper set of spin wave branches. For the best fit we find that $J_{F2} = 0.93 \pm 0.02\text{ meV}$ and $J_{F3} = -0.97 \pm 0.02\text{ meV}$.

A particular difference between PCMO and PCSMO is that in the former the coupling between CE planes is expected to be significant, whereas in the latter it is rather small. Indeed, previous low energy INS measurements of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (ref. 22), which one would expect to be similar to PCMO, found that the inter-plane coupling was about a factor of four larger than the coupling between zig-zag chains. The complex twinning, together with an intermediate strength coupling between
CE planes, means there is not a single feature which can be used to determine $J_e$ easily. The strength and position of the signal around $(\pm 0.5, 0)$ at $\sim 22$ meV in Fig. 2(a), with $E_i = 35$ meV, exhibits qualitative dependence on $J_e$, but overall the best method for refining $J_e$ is to use all of the data when performing the final global fit. We found $J_e = -2.09 \pm 0.03$ meV, which like in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ is about a factor four larger than the in-plane antiferromagnetic coupling between zig-zag chains.

In the above, we set the charge disproportionation between notional Mn$^{3+}$ and Mn$^{4+}$ sites, which is known to be substantially smaller than the ideal value and closer to Mn$^{3.4+}$ and Mn$^{3.6+}$, to be zero in order to simplify the analysis. This meant that all spins were set to an average value of $S = 7/4$. The effect of charge disproportionation would be to have different values of the spin on alternate Mn sites along the zig-zags, which would halve the real-space periodicity and thereby open up a gap to create lower and upper dispersion branches, even with $J_{F2} = J_{F3} = 0$. However, the observed gap can only be reproduced by having charge disproportionation of Mn$^{2.8+}$ and Mn$^{4.2+}$, several times larger than typical values observed using other techniques. If we use a typical value of $\pm 0.1e$ for the charge disproportionation, this only accounts for $1/7$ of the observed gap, and we can only account for the majority of the gap with slightly reduced $J_{F2}$ and $J_{F3}$.

B. Zener polaron model

Let us now turn to the ZP model. As shown in Fig. 2, a key feature that distinguishes the CE and ZP models is the presence or absence of a second band of excitations. By far the dominant exchange constant in the ZP model is expected to be that within the dimers. Accordingly, we expect one set of spin wave branches associated with coupling of the rigid ZP dimers that will have a band width determined by the characteristic inter-dimer exchange energies. These will be separated from a second set of branches associated with excitation of the pair of spins within the ZP by an energy gap determined by the much stronger intra-dimer exchange. That is, we expect a gap that could be several multiples of the bandwidth of the lower energy set of spin wave branches, which in the limiting case of the ratio of intra-dimer to inter-dimer exchange tending to infinity eliminates half the spin wave branches. In contrast, the CE model permits a small (or even zero) gap between two sets of branches depending on the existence (or otherwise) of second neighbor interactions along the ferromagnetic zig-zag chains. As illustrated in Fig. 2, judicious choice of $J_A$, $J_{FU}$ and $J_{FD}$ in this limiting ZP model (the model shown in Fig. 2(b)) results in spin wave branches that closely follow the lower energy half of the CE branches, but in general the reverse is not possible. This is because the limiting ZP model has only half the number of spin wave modes by virtue of the rigid coupling of spins within the dimers.

Moreover, the periodicity of the most energetic branch in our data corresponds to the nearest-neighbor Mn–Mn distance projected along the direction of the zig-zags. The nearest-neighbor separation of ZP dimers is twice that, which would result in a doubling of the periodicity of the spin wave branch compared to what we observe. In summary, because we have been able to measure the higher energy branches, which are separated from the lower branches by a relatively small gap, we are able to discount a model of weakly interacting dimers without making assumptions about the relative magnitudes of $J_A$, $J_{FU}$ and $J_{FD}$. In fact, this conclusion should apply to any case of interacting dimers, so long as the intra-dimer exchange is dominant over all other interactions (nearest neighbor and further neighbor) between a spin in one dimer and those in other dimers.

C. Dimer model

Rather than considering a model of weakly interacting dimers, an alternative is to consider one in which pairs of spins are dimerised in a fashion similar to that proposed in the ZP model, but without the intra-dimer exchange being dominant. Such a model was discussed by Johnstone et al in their work on PCMO, and is shown in Fig. 1(c). The rationale is that the dominant exchange is the FM nearest-neighbor interaction along the zig-zags, but allowing for a small modulation between weaker and stronger exchange will create a gap at $(1/2, 0)$ by virtue of doubling the repeat distance along the zig-zags. In PCSMO, with a suitable choice of parameters, this model produces an essentially indistinguishable dispersion relation to the CE model, but the two models can be distinguished by differences in the structure factor at the top of the lower branch of the dispersion.

However, this weak dimer model is in fact a special case of a more general weak dimer model, shown in Fig. 4(d), and which we will use in the following discussion. We allow for alternating stronger and weaker nearest-neighbor FM exchange within the zig-zags, but for the time-being disallow the next nearest neighbor exchange $J_{F2}$ and $J_{F3}$. In order to anticipate the relationship and likely signs of the exchange constants between adjacent zig-zags, let us suppose that since the measured charge disproportionation is small, the Mn orbitals all have the symmetry of $d_{3z^2-r^2}$ orbitals, and with the lobes on the two Mn sites within a dimer pointing at each other to give strong ferromagnetic exchange coupling via the double exchange mechanism. In Fig. 1(d) one can see that each Mn ion has one nearest-neighbor within the same dimer as itself (we shall refer to this as dimer A), and three other nearest-neighbor Mn ions in different dimers. One of these three dimers is oriented parallel to dimer A, whereas the other two dimers are perpendicular to dimer A. The Mn–O–Mn bond angles in PCMO are not far from 180° (refs. [12] and [13]), so following the Goodenough-Kanamori rules, we expect...
AFM coupling between nearest-neighbor Mn ions in parallel dimers, and FM coupling between nearest-neighbor Mn ions in perpendicular dimers. We therefore denote the AFM interaction between nearest-neighbors in parallel dimers with the exchange parameter $J_A$, and the weak FM interaction between nearest-neighbors in perpendicular dimers with the exchange parameters $J_{FW1}$, $J'_{FW1}$, $J_{FW2}$ and $J'_{FW2}$. We have allowed four different weak ferromagnetic exchange because of four different Mn–O–Mn bond angles affecting the two different Mn ions that have different crystallographic site symmetry.\cite{footnote} In principle these different bond angles modify the superexchange coupling. This model differs from that proposed by Johnstone et al, in which $J_{FW1} = J'_{FW1} = J_{FW} > 0$, and $J_{FW2} = J'_{FW2} = J_A2 < 0$, i.e. the dimer model shown in Fig. (c) is a limiting case of the more general model shown in Fig. (d).

Analyzing our data using the dimer model we found that, as for PCSMO, it is possible to reproduce the same dispersion as obtained from the CE model with best fit parameters. We fitted the dimer model in the same manner as the CE model, described above, obtaining estimates for the strong intra-dimer coupling $J_{FS}$ from the highest-energy part of the dispersion. Estimates for the weaker inter-dimer couplings were determined from low-energy features of the data and from the size of the gap between the upper and lower spin wave branches. The size of the gap is mostly determined by the difference between the intra- and inter-dimer coupling, with the relatively narrow gap of $\sim 5$ meV indicating a relatively weak dimerization. Although in principle $J_{FW1} \neq J'_{FW1}$, we found that in practice a difference between these parameters introduced a further gap in the dispersion in the middle of the high-energy branch, a feature not evident in the data. In order to reproduce the observed dispersion we found that $J_{FW2} \ll J_{FW1}$, and that splitting $J_{FW2}$ and $J'_{FW2}$ seemed to have little effect. We therefore constrained our fits to have $J_{FW1} = J'_{FW1}$ and $J_{FW2} = J'_{FW2}$.

The dimer model parameters were then refined using the same cuts as were used for the refinement of the CE model parameters. The best fit parameters were then $J_{FS} = 10.74 \pm 0.03$ meV, $J_{FW1} = J'_{FW1} = 7.02 \pm 0.04$ meV, $J_{FW2} = J'_{FW2} = 1.26 \pm 0.11$ meV, $J_A = -2.47 \pm 0.14$ meV, and $J_c = 2.19 \pm 0.03$ meV. This produces an essentially identical dispersion relation to that obtained from the best fit parameters to the CE model.

The small size of the gap between the spin wave branches compared to the overall bandwidth is reflected by rather weak dimerization, quantified by $J_{FS}$ being only 53% larger than $J_{FW1}$. It is therefore not surprising that both $J_{FS}$ and $J_{FW1}$ are quite close in value to $J_{F1}$ in the CE model, since they are largely determined by the maximum energy of the dispersion. As an aside, an interesting difference between the CE and dimer models is in the nature of the AFM coupling between the zig-zag chains. The AFM coupling in the dimer model is a factor $\sim 5.5$ larger than in the CE model. This can be understood by noticing that $J_A$ is used for the exchange pathways in the CE model that are described by $J_{A1}$ and $J_{FW2}$ in the dimer model. In order for the same magnetic structure to be stable in the dimer model, $J_{A1}$ has to be much larger than $J_{FW2}$, since there are two AFM contributions ($J_A$) to the total energy in the CE model, balanced against one AFM contribution ($J_{A1}$) and one FM contribution ($J_{FW2}$) in the dimer model. These last two terms effectively trade against one another to give an overall antiferromagnetic interaction between zig-zags and identical dispersion to that observed in the CE model. The interaction between the planes that contain the zig-zag chains, $J_c$, is almost the same for the dimer and CE models, since this term describes the same physics in both cases.
The structure factor at \((0,0)\) terms along the zig-zags. While the absence of peaks in the \((0,0)\) and \((1/2,0)\) and \(35\text{meV}\) to be accounted for by allowing alternative neighbor exchange interactions along the zig-zags, the latter accounts for it using further neighbor interactions are permitted. Adding to the dimer model the same further neighbor terms that were used in the CE model, \(J_{F^2}\) and \(J_{F^3}\), and repeating our analysis, we found that the amount of dimerization (the difference between \(J_{F^2}\) and \(J_{FW^1}\)) reduced from 53\% to \(\sim 17\%\). The weak alternating exchange (17\%) along the zig-zags in this fit is likely because there are more degrees of freedom available to fit the data compared to the CE model. As before, the sum \(J_{FW^2}+J_{A1} \rightarrow 2J_A\). Adding further neighbor exchange interactions to the dimer model therefore transforms it essentially into the CE model.

V. CONCLUSION

In conclusion, we have studied the spin waves in PCMO using ToF neutron spectroscopy and found that the upper and lower branches of the dispersion are gapped. This is consistent with the CE model with strong nearest-neighbor ferromagnetic interactions along the zig-zag chains and weak antiferromagnetic interactions between them, provided there exist small next-nearest-neighbor couplings along the zig-zags. The gross features of the spin wave dispersion allow us to rule out the Zener polaron picture in the limit of strongly bound dimers as a description of the ground state of PCMO. An alternative model in which pairs of spins are weakly dimerized, is shown to provide a better description of the data than the Zener polaron model itself, however subtle differences between this model and the data are still observed. These subtle differences do not arise in the CE model, so our data indicate that the CE model with significant second neighbor interactions within the FM zig-zags provides the most satisfactory description of the magnetic ground state of PCMO. These conclusions are very similar to those recently drawn for the bilayer variant PCSMO\(\text{II}\), suggesting a common description of the half-doped CO ground state in favor of the CE picture rather than ZP picture, at least in the magnetically ordered phase.

We found that the nearest neighbor FM interaction along the zig-zags is comparable or larger than the typical values found for the FM exchange in metallic manganites, suggesting a common origin in the double exchange mechanism. The significant further neighbor interactions are suggestive of delocalization of the \(e_g\) electrons. These results are consistent with the theoretical analysis of the degenerate double exchange (DDEX) model for half-doping\(^{39,40}\). In this model, a cooperative ordering of the charge and degenerate \(e_g\) orbital degrees of freedom takes place to accommodate the frustration between delocalization (which favors ferromagnetism) and the antiferromagnetic superexchange between the core \(t_{2g}\) moments. The result is FM zig-zag chains that are antiferromagnetically coupled. For \(x = 0.5\) charge modulation of \(\lesssim 0.1\)\text{e} is site centered so that all Mn–Mn bonds along the zig-zag are identical. The DDE\(X\) model ignores the effects of the errorbars on the data points.

One might be tempted to conclude that because the dispersions obtained from best fits to both the CE and dimer models are essentially indistinguishable, the models are equivalent. In fact this is not the case. For most of the energy scale of the excitations the two models have very similar structure factors. However we find that near the top of the lower spin wave branch the structure factors are different, and are readily distinguished on examination of the data along a well-chosen symmetry direction, perpendicular to the zig-zag chains. This difference in structure factor between the data and CE model, and the dimer model, is illustrated in Fig. \(7\). The agreement between the data and CE models (panels (a) and (b)) is good, but there is enhanced intensity around the \((0.5,0,1)\)-type positions arising from a larger structure factor from the dispersion which converges on these points in the dimer model (panel (c)) which does not agree with the data. To quantify this difference further we show in Fig. \(8\) a 1-dimensional cut through the data along a well-chosen symmetry direction, perpendicular to the dimer model global best fit, that fails to do so. The differences are clearly statistically significant, since the difference between the dimer model and the data at the \((0.5,0,1)\)-type positions is much larger than the size of the errorbars on the data points.

The essential physical difference between the dimer and CE models is that the former allows for the gap at \((1/2,0)\) and \(35\text{meV}\) to be accounted for by allowing alternating nearest-neighbor FM exchange along the zig-zags, whereas the latter accounts for it using further neighbor terms along the zig-zags. While the absence of peaks in the structure factor at \((0.5,0,1)\) shown in Fig. \(5\) strongly support the CE model, a question which naturally arises is what is the result if both weak dimerization and further neighbor interactions are permitted. Adding to the dimer model the same further neighbor terms that were used in the CE model, \(J_{F^2}\) and \(J_{F^3}\), and repeating our analysis, we found that the amount of dimerization (the difference between \(J_{F^2}\) and \(J_{FW^1}\)) reduced from 53\% to \(\sim 17\%\). The weak alternating exchange (17\%) along the zig-zags in this fit is likely because there are more degrees of freedom available to fit the data compared to the CE model. As before, the sum \(J_{FW^2}+J_{A1} \rightarrow 2J_A\). Adding further neighbor exchange interactions to the dimer model therefore transforms it essentially into the CE model.
of coupling to the lattice degrees of freedom or disorder, so cannot account for any cooperative distortion of the MnO$_6$ units with corresponding alteration of the $e_g$ orbital occupancies that could result in magnetic dimerization, such as that proposed for Pr$_{0.8}$Ca$_{0.2}$MnO$_3$\textsuperscript{15}. However, our results indicate that any such distortion does not affect the magnetic exchange interactions, and that the magnetic degrees of freedom are best described by the CE model within the DDEX picture.

We are grateful to A. Daoud-Aladine, G. A. Sawatzky, J. P. Hill and F. Krüger for helpful discussions, and to A. J. Wenban for work on the dimer spin wave model. This work was supported by the Science and Technology Facilities Council of Great Britain. OS acknowledges financial support from the Engineering and Physical Sciences Research Council of Great Britain, and from the Okinawa Institute of Science and Technology. This research at Oak Ridge National Laboratory’s Spallation Neutron Source was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences.

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This is the convention used in ref. 13. PCMO is usually described in terms of the orthorhombic space group $Pnma$, in which the lattice parameters are related to those of the pseudocubic perovskite $a_{P}$ by $a \approx c \approx \sqrt{2}a_{P}$, $b = 2a_{P}$. We use the $Pbnm$ convention here in, with $a \approx b \approx \sqrt{2}a_{P}$, $c = 2a_{P}$, in order to be consistent with the study of bilayer PCSMO by Johnstone et al.\textsuperscript{15}.

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