Influence of interstitial Mn on magnetism in room-temperature ferromagnet Mn$_{1+\delta}$Sb

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We report elastic and inelastic neutron scattering measurements of the high-$T_C$ ferromagnet Mn$_{1+\delta}$Sb. Measurements were performed on a large, $T_C = 434$ K, single crystal with interstitial Mn content of $\delta \approx 0.13$. The neutron diffraction results reveal that the interstitial Mn has a magnetic moment, and that it is aligned antiparallel to the main Mn moment. We perform density functional theory calculations including the interstitial Mn, and find the interstitial to be magnetic in agreement with the diffraction data. The inelastic neutron scattering measurements reveal two features in the magnetic dynamics: i) a spin-wave-like dispersion emanating from ferromagnetic Bragg positions (HK2n), and ii) a broad, non-dispersive signal centered at forbidden Bragg positions (HK2n+1). The inelastic spectrum cannot be modeled by simple linear spin-wave theory calculations, and appears to be significantly altered by the presence of the interstitial Mn ions. The results show that the influence of the interstitial Mn on the magnetic state in this system is more important than previously understood.

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INTRODUCTION

Mn$_{1+\delta}$Sb is a high Curie temperature ($T_C$), highly anisotropic, metallic ferromagnet. The observation of a ferromagnetic state in Mn$_{1+\delta}$Sb is unusual in its class of materials. Most Mn-alloys are antiferromagnetic, and other 3d transition metal mono-antimonides are not ferromagnetic — CrSb, FeSb and CoSb are antiferromagnetic, TiSb is paramagnetic and NiSb is diamagnetic. The ferromagnetic state in Mn$_{1+\delta}$Sb is highly sensitive to substitutions; for example, Cr-doping quickly tunes the system towards an antiferromagnetic state. In-fact substitutions of the cation, the anion, or presence of an interstitial can each alter $T_C$, the magnetic anisotropy, or the type of magnetic order. This potential for tuning the properties in Mn$_{1+\delta}$Sb, and closely related Mn$_{1+\delta}$Bi, has attracted considerable attention because the materials show promise as alternatives to rare-earth containing permanent magnets, and as magneto-optic mediums.

The spontaneous magnetization in Mn$_{1+\delta}$Sb is along the crystallographic c-axis at high temperatures. However, the anisotropy decreases on cooling and passes through zero at the spin reorientation temperature, $T_{SR}$, so that the magnetization is in-plane at low temperatures. In nominally $\delta = 0$ polycrystalline MnSb the $T_C$ is as high as $T_C = 587$ K. However, single crystal studies have been unable to produce the material without the inclusion of interstitial Mn ions. These interstitial Mn ions, Mn2, are present in addition to the fully-occupied main site Mn ions, Mn1. The Mn2 ions are hosted within the hexagonal NiAs crystal structure as shown in Fig. 1(d). Compositions in the range of $\delta \approx 0.05 - 0.2$ have been found to be stable.

The presence of interstitials significantly alters the properties of Mn$_{1+\delta}$Sb. As $\delta$ increases, the a lattice parameter and unit cell volume increase, but the c lattice parameter, $T_C$, $T_{SR}$ and the total magnetization decrease. Studies combining magnetization measurements with chemical analysis found that the interstitial Mn results in a reduction of the ferromagnetic ordering temperature as captured in a simple relationship between $T_C$ and $\delta$:

$$T_C = (577 - 900 \times \delta) K. \quad (1)$$

The electronic structure and magnetic state of Mn$_{1+\delta}$Sb have been investigated by a number of authors via electronic structure calculations. They found that MnSb is described as a metallic system with localized magnetic moments, and show that the ferromagnetic state is stabilized due to the significant hybridization between the Mn 3d and Sb 5p orbitals. All these calculations, however, have failed to describe key experimental observations such as the behavior of the magnetic anisotropy, and the effect of the interstitial Mn on the magnetic properties, explicitly in their models. Coehoorn et al. simply discuss Mn2 as an electron doner, and were unable to explain its influence on the magnetic properties.

Given the importance of the interstitials in tuning the properties of Mn$_{1+\delta}$Sb, it is surprising that detailed theoretical investigations of the effect of Mn2 are lacking. Experimental results are also limited, and have focused on the empirical determination of the $\delta$ dependencies of
We use neutron diffraction to measure a large number of Bragg peaks from a single crystal. We identify a spin-wave-like signal, but, unlike $\delta = 0$ MnBi, we are unable to fully describe its dispersion using a simple, localized-moment Heisenberg model, suggesting the ferromagnetic excitations are modified due to the presence of Mn2. In addition to the spin-wave-like scattering, we also identify a broad, intense, magnetic response in the inelastic spectrum. This signal is not observed in MnBi, and therefore is likely attributable to the presence of the disordered interstitials in Mn$_{1.13}$Sb. These results highlight the strong influence that the presence of the interstitial Mn has on the magnetic properties of Mn$_{1+\delta}$Sb.

**EXPERIMENTAL TECHNIQUES**

The single crystal of Mn$_{1+\delta}$Sb used in this investigation is the same $\sim 6 \text{cm}^3$ crystal that was studied in Ref. [31]. Pieces taken from the large crystal were used for diffraction and magnetization measurements.

To determine the spin reorientation temperature, a piece of the crystal was aligned at room temperature to within $15^\circ$ of the easy axis (c-axis) using a permanent magnet. The magnetization ($\mathbf{M}$) was then measured in a Quantum Design Magnetic Property Measurement System, with applied fields $\mathbf{H}$ either parallel or perpendicular to this axis. This measurement clearly reveals a spin reorientation temperature of $\sim 160 \text{K}$, as shown in Fig. 2(a). The same crystal was then used to obtain the Curie temperature of 434 K, see Fig. 2(b). This high-temperature measurement employed the Sample Space Oven from Quantum Design, which utilizes thin quartz holders that precluded alignment of the crystal. Here, we have defined $T_C$ as the intercept of the greatest tangent to the $\mathbf{M}/\mathbf{H}$ versus $T$ data, with the greatest tangent being observed at 423 K. According to Eq. 4, $T_C = 434 \text{K}$ gives an interstitial content of 16%, consistent with the value predicted from the lattice parameters in Ref. [31]. With an applied field of 6 T, the moment is essentially saturated at 2 K, and for $\mathbf{H} \perp c$ we measure a saturated moment of $3.20 \mu_B/f.u.$, where f.u. is a formula unit Mn$_{1.13}$Sb. The high-temperature data shows a minor onset of magnetization magnetization at $T \sim 580 \text{K}$, see Fig. 2(b). This is likely associated with a small close-to-stoichiometric MnSb impurity, or a small amount of some unknown phase.

Neutron diffraction measurements were performed on...
RESULTS

Results from the neutron diffraction measurements are shown in Fig. 1. The temperature dependencies of (1 1 0) and (1 0 2) Bragg reflections across $T_C$ and $T_{SR}$ are shown in Fig. 1(a) and (b), respectively. These reflections have structure factor contributions from all three atoms in the unit cell. The intensities of these Bragg peaks respond to both $T_C$ and $T_{SR}$, indicating that they are magnetic Bragg reflections, and confirming the identification of $T_C$ and $T_{SR}$ from magnetization. Figure 1(c) shows the (1 0 3) Bragg reflection at 443 K and 10 K. The Mn1 site in the NiAs crystal structure has the reflection condition $l = 2n$, where $n$ is an integer. Therefore, the (1 0 3) peak has zero nuclear contribution to its structure factor from Mn1, and also zero magnetic contribution if the magnetic form factor of Mn1 is spherical. Both Mn2 and Sb ions contribute scattering intensity to the (1 0 3) reflection.

To determine the origin of the increased intensity at low temperature of $l = odd$, $(h-k) \neq 3n$ Bragg peaks, we investigated two possible models for the magnetic state in Mn$_{1+\delta}$Sb for all reflections collected. Both models use the NiAs structure, hexagonal space group P6$_3$/mmc (No. 194), which has two formula units of Mn$_{1+\delta}$Sb per unit cell, with Mn1 on the 2a Wyckoff site, Sb on the 2c Wyckoff site, and Mn2 on the 2d Wyckoff site. Recent x-ray diffraction results from the closely related compound MnBi identify a slight distortion from hexagonal symmetry below $T_{SR}$, however the resolution of our neutron diffraction measurement is not sufficient to detect a distortion of this size. The difference between the two models we investigate concerns the magnetic component of scattering below $T_C$.

The first model comprises a ferromagnetic arrangement of Mn1 moments, with Mn2 moments aligned antiparallel to Mn1. A depiction of this model is shown in Fig. 1(d) for $T < T_{SR}$, i.e. with spins aligned within the a-b plane. For $T > T_{SR}$ the Mn1 and Mn2 moments are aligned along the c-axis, but still antiparallel to each other. The 3d-5p hybridization is expected to induce a small moment on the Sb site antiparallel to Mn1 [24]. However, considering the expected moment size and the steep magnetic form factor for Sb 5p electrons [25], the overall contribution of Sb to the magnetic diffraction pattern is expected to be small. Therefore we do not include magnetic intensity from Sb in the fitting for either model 1 or model 2, consistent with previous reports [26,27]. As Sb and Mn2 have the same reflection conditions, this may have the effect of slightly increasing the moment size assigned to the interstitial Mn.

The model was fit to the data using Rietveld refinement in the FullProf software suite [34]. For a random distribution of interstitial Mn ions, the average structure can be modeled by assuming a uniform distribution of Mn2 on every 2d Wyckoff site and scaling the scattering intensity by the occupancy $\delta$. The atomic displacement parameters for Sb and Mn2 were constrained to be equal, as they contribute to the same reflections. The initial fit
was performed against the $T = 450 \text{ K}$ (i.e. $T > T_C$) data set, allowing us to determine the interstitial content of the sample without the influence of magnetic Bragg scattering. This gave the result $\delta = 0.13(1)$, which is reasonably close to the value estimated from comparison to the magnetic scattering measurement (see Fig. [2]) to Eq. [1]. For subsequent fits of the magnetic model against 10K and 200K data sets the interstitial content and the extinction parameter were kept fixed. The magnetic form factor of Mn$^{2+}$ was used. For the 10K data set, the model included three domains in equal proportions with spins along $a$, $b$, and $[-1 -1 0]$ directions respectively. The results of these fits are summarized in Fig. [3(a), (c) and (d) and Table [1]. Excellent agreement between data and model 1 is found. Attempts to fit an interstitial Mn moment aligned parallel to Mn1 were unsuccessful. The model with an antiparallel moment on the Mn2 site describes the data for the entire range of $Q$ and temperature measured.

The second model is based on that proposed by Haneda et al. [23] for MnAs and discussed in detail for MnSb by Yamaguchi et al. [25]. in which Mn2 does not have a magnetic moment associated with it. In this case, they explain the observed magnetic scattering at $(103)$ and other $l=\text{odd}$ Bragg positions using a highly aspherical magnetic form factor for the main site Mn. Having an aspherical magnetization density breaks the symmetry conditions that normally result in systematic absences for $l=\text{odd}$ reflections from the $2a$ Wyckoff site, allowing intensity at $l=\text{odd}$, $(h-k) \neq 3n$ positions. The model includes the combined scattering intensity for structural contributions from all ions, plus the magnetic intensity from the Mn1 ions for all reflections. The overall structure factor resulting from the Yamaguchi model, with adjusted interstitial content and electron occupancies to match our data, is compared to the 10K data in Fig. [3(b)]. At high $Q$ there is good agreement between model 2 and our data, however at low $Q$ the model deviates significantly from the observed scattering intensity. Therefore model 2 is not as effective as model 1 in describing the results of our neutron diffraction experiment. This will be examined further in the Discussion Section.

To gain a better understanding of the influence of the Mn interstitials on Mn$_{1+2}$Sb we performed DFT calculations including an interstitial in the unit cell (see [27] for technical details). First we readdress the question of whether the interstitial Mn has a magnetic moment, and if so how it is directed with respect to the ferromagnetically aligned moments of the host Mn atoms. To this end we considered the $2 \times 2 \times 1$ supercell Mn$_8$Sb$_8$ depicted in Fig. [1] which contains a single interstitial Mn atom. To account for the influence of Coulomb interactions among the Mn-3d electrons we use the PBE+U approximation, and vary the Hubbard $U$ parameter between 0 and 8eV. For all cases, we find that it is not possible to stabilize a configuration in which the interstitial Mn is non-magnetic. The tables in Fig. [2] show that for $U = 0$, 2 and 4eV the configuration with Mn2 aligned parallel to Mn1 is higher in energy than the configuration in which it is aligned antiparallel, consistent with the results from neutron diffraction. For $U = 6$ and 8eV, however, the configuration with the parallel alignment of the interstitial Mn is energetically favored. It is reasonable to expect that the Coulomb d-d interactions are at the lower end of the scale, given that the very large wave functions of the Sb 5p electrons can effectively screen the transition metal interactions. Related to this, we find for all cases that the system remains metallic, even for a Hubbard $U$ of 8eV.

Next we examine the effect of the Mn interstitials on the ferromagnetic configuration of the host Mn moments. To investigate the stability of the ferromagnetic ground state (FM) we compare its energy with that of two higher energy configurations in which the atomic positions remain unchanged, but the host Mn moments assume an antiferromagnetic configuration either along the c-axis (AFM-c) or the a-axis (AFM-a) as shown in Fig. [5] Comparing Fig. [5(a) and (c)], the presence of the Mn interstitial lowers the energy difference between the FM ground state and the high energy AFM configurations. The energy difference between the FM and the AFM-c configuration reduces quite significantly from 286 to 212meV and the energy difference between the FM and the AFM-a configuration decreases from 326 to 306meV. The results in Fig. [5] are for a $U = 2$eV, but for a $U$ of 8eV we find that this qualitative conclusion remains unchanged [38].

It is important to note that the simulations in Fig. [5(a) and (c)] include the indirect influence of Mn2 via their in-
A table showing the results from Rietveld refinements fitting model 1 to the data. Vol. is volume of the unit cell, $M_{Mn1}$ and $M_{Mn2}$ are the magnitudes of the magnetic moments on Mn1 and Mn2 sites respectively, $\chi^2$ and $RF$ are the statistical agreement factors determined by FullProf. $\chi^2$ is low for the 450K data set because of the shorter collection time used for this data set. The errors on the moment sizes are the estimated standard deviation calculated by FullProf.

Figure 4. (Color online) The optimized lattice constants, the average host Mn1 moment, the interstitial Mn2 moment, the average Sb moment, and the total energy per interstitial Mn2 atom of the parallel (P) and antiparallel (AP) configuration of Mn2 calculated within the PBE+U approximation for U=0,2,4,6 and 8 eV.

Figure 5. (Color online) The lattice constants, the average of the magnetic moments on Mn1 and Mn2 sites respectively, $M_{Mn1}$ ($\mu_B$) $M_{Mn2}$ ($\mu_B$) $E$(meV) per Mn2Sb, for the FM, AFM-c and AFM-a configurations for the cases without Mn2, giving effective strained lattice constants. With Mn2, we performed INS experiments to probe the magnetic dynamics. An overview of the results from SEQUOIA is given in Figs. 6(a) and 7 which show HL-plane and QE-plane color maps, respectively, as well as constant-energy cuts through the data in Fig. 7(d).

Table I. Results from Rietveld refinements fitting model 1 to the data. Vol. is volume of the unit cell, $M_{Mn1}$ and $M_{Mn2}$ are the magnitudes of the magnetic moments on Mn1 and Mn2 sites respectively, $\chi^2$ and $RF$ are the statistical agreement factors determined by FullProf. $\chi^2$ is low for the 450K data set because of the shorter collection time used for this data set. The errors on the moment sizes are the estimated standard deviation calculated by FullProf.
rings of scattering in the HL plane are seen dispersing with energy out of the ferromagnetic positions such as (100) and (002). These rings persist above both \(T_{SR}\) and \(T_C\). The intensity of this scattering is rapidly suppressed with increasing \(Q\), and it persists up to energies of \(\sim 70\) meV (see Fig. 7(a)), well above the phonon cutoff of \(\sim 30\) meV, indicating the magnetic origin of the signal. A qualitatively similar signal is observed in MnBi [30], which contains no interstitial Mn, see Fig. 6(b).

In addition to the spin-wave type signal, a broad signal is evident between the rings in the HL plane at all temperatures, see Fig. 6. This broad signal was not observed in MnBi, corroborating that it is a distinct feature of the excitation spectrum of Mn$_{1+\delta}$Sb. The broad signal is centered on (001) and equivalent positions. The (001) is not an allowed Bragg reflection in this system, and no Bragg peak was observed at this position in any of the measurements we performed. Figure 7(c) highlights that this signal is broad but localized in \(Q\)-space, and seemingly non-dispersive. Again, the intensity suppression with \(Q\) and the energy range of the signal both indicate that it is magnetic in origin. This signal was previously observed at the (101) (which is a Bragg peak position) in the triple-axis-spectroscopy work of Radhakrishna and Cable [31], but we have now been able to map its full \(Q\) and \(E\) dependence and confirm the signal’s magnetic origin, in addition to observing it at (001).

Further investigation of the scattering centered on (001) is presented in Fig. 9. Cuts taken along (10L) and (H01) directions through datasets collected at 10 K, 350 K and 443 K are shown in Fig. 9(a) and (b). As the (H01) direction is the zone boundary for the spin wave signal, the cuts in Fig. 9(b) and the color map in Fig. 9(c) essentially show the broad signal in isolation. The (10L) direction, however, passes through the zone center for both the spin wave and the broad signal, see Figs. 9(a) and 9(d). We show the temperature dependence of the (001) signal in Fig. 9(c). The integrated intensity was determined from cuts made along the (H01) direction through the limited-angular-range data measured at \(E_i = 150\) meV for all temperatures. The data were averaged over 10–20 meV and folded along H and L to improve statistics. Two Gaussian functions on a flat background were fit to the data, with widths constrained to be equal, but amplitudes varying independently, and centers fixed at \(H=0\) and \(H=1\). The resulting area of the Gaussian centered at \(H=0\) was corrected for the Bose population factor, \([1-\exp(-E/k_B T)]^{-1}\), at each temperature and the result gives the integrated intensity plotted in Fig. 9(c).

These results show that the broad, \(Q = (001)\)-centered scattering is influenced by \(T_{SR}\), Fig. 9(c). There is a dramatic increase in intensity of the signal on warming past \(T_{SR}\), which is expected for scattering from a transverse magnetic fluctuation as the spins reorient from \(ab\)-plane to \(c\)-axis alignment, because the magnetic cross section depends only on the component of the magnetic moment perpendicular to \(Q\). This is further supported by the observation that the (001) scattering is more sensitive to \(T_{SR}\) than the scattering at (±101), compare the cuts in Fig. 9(b). These observations are a further confirmation of the magnetic origin of the signal, and indicate coupling between this scattering and the ferromagnetic state of the system.

We attempted to model the inelastic magnetic response of the system using linear spin-wave theory. Isotropic exchange interactions including up to sixth nearest neighbors were the minimum required to model the spin-wave frequencies. The six nearest neighbor exchange parameters, \(J_S\), are illustrated in Fig. 9(c). Single-ion anisotropy was not included because there was no evidence for a gap in the spin wave spectrum down to at least 0.5 meV (< 1% of the bandwidth), see Fig. 10. The data from CTAX shows that the dispersion of the magnetic signal along \(H\) can already be observed out of (100) with an energy transfer of 0.5 meV, see Fig. 10. The inelastic neutron cross section for undamped spin waves was calculated using the \(1/S\) formalism outlined in Ref. [39] and appendix A of Ref. [40].

For comparison with experimental intensities, the effects of the magnetic form factor and an approximation for the instrumental resolution were included in the calculation. We used the magnetic form factor for Mn$^{2+}$ from Ref. [35]. The resolution function was approximated as a Gaussian in energy with a full width at half-maximum of 7.5 meV and the results averaged over the same volume of \(Q\) as the experimental data (Fig. 7) and averaged over six domains. To determine the exchange parameters, the model was fit to the dispersions along (100), (001) and (110) directions, extracted from the experimental data via a series of constant-energy cuts and fits like those in Fig. 9(d). We determined the energy at the (H02) zone boundary, 70(4) meV, by fitting a Gaussian to a constant-\(Q\) cut at (1.502) from which a similar cut at (202) had been subtracted as a background.

Only \(J_0\) can be uniquely determined from our results. Instead, the linear combinations

\[
\alpha = J_1 + 6J_3 \\
\beta = J_4 + 6J_5 \\
\gamma = J_2 + 2J_3 + 2J_5
\]

were fit. The values best fitting these measurements are \(\alpha S = 20.0\) meV, \(\beta S = -0.8\) meV, \(\gamma S = 4.8\) meV, and \(J_0 S = 2.9\) meV. Fig. 8 shows the calculated frequencies and intensities along two of the measured directions, for comparison to Fig. 7(a) and (b). Previously Refs. [31] and [30] reported triple-axis spectroscopy measurements on Mn$_{1+\delta}$Sb which covered limited ranges of \(Q\) and \(E\), not reaching the zone boundary. In Ref. [31] they fit a Heisenberg model up to fourth nearest neighbors (i.e. \(J_5, J_6 = 0\)) to the low energy data measured on a Mn$^{2+}$Sb crystal. They found \(\alpha S = 8.75\) meV, \(\beta S = 2.4\) meV and \(\gamma S = 5.4\) meV. These results extrapolate to a bandwidth of 130 meV along (H02), which is much larger than the 70(4) meV we observe, see Fig. 7.
DISCUSSION

The results of our neutron diffraction experiment on Mn$_{1.13}$Sb are well described by the magnetic structure shown in Fig. 1(d), with ferromagnetic alignment of Mn1 ions, and Mn2 ions aligned antiparallel to Mn1. There appears to be no need to include the model of an aspherical form factor for Mn1 to account for magnetic scattering at $l = \text{odd}$, $(h-k) \neq 3n$ Bragg peak positions for our data set. This is consistent with early neutron powder diffraction results on Mn$_{1+\delta}$Sb [27], but in contrast to the interpretations of Yamaguchi et al. [25] and Reimers et al. [26] from their polarized-neutron, single-crystal experiments.

The single crystals investigated in Refs. 25 and 26 were of composition Mn$_{1.05}$Sb and Mn$_{1.09}$Sb respectively, lower interstitial contents than our crystal, and in both cases they excluded some low $Q$ data from their analysis. This may explain the seeming discrepancy between their interpretation and our results. In the former case, the scattering from Mn2 sites would have been weaker, and therefore harder to interpret. The higher $Q$ data that they included in their analysis is less sensitive to magnetic scattering from the interstitial site, but more sensitive to the asymmetric form factor they describe. In the case of our data, either model adequately describes the high $Q$ data, but only the model including an antiparallel moment on Mn2 can account for all peaks observed below $T_C$ across all $Q$, see Fig. 3(a) and (b). Our data is less sensitive to any asymmetry in the Mn1 form factor because it was not a polarized neutron measurement and the magnetic contribution at high $Q$ is small. We benefited from modern Rietveld refinement software, in combination with a large dataset and a higher interstitial content, to show that model 1 with a moment on Mn2 describes our data over the entire range of $Q$. Our results do not preclude some asphericity in the magnetic form factor of Mn1. It is likely, however, that the asphericity found in the previous models is too large, as some of the scattering intensity should have been accounted for by the moment on Mn2. This helps to explain the discrepancies between the Yamaguchi model [25] and results from x-ray Compton profile analysis [29], and electronic structure calculations [12], as well as the failure of the model at low $Q$ [20, 25, 26].

The size of the magnetic moments found from our FullProf refinement of model 1 are consistent with magnetization measurements. The saturated moment per formula unit was found to be 3.20 $\mu_B$ at 2 K from magnetization. The results from HB-3A give a total moment per formula...
Figure 7. (Color online) (a-c) Neutron scattering intensity maps for Mn$_{1+δ}$Sb from data taken on SEQUOIA with $E_i = 150$ meV at 10 K. The data were averaged over ±0.1 r.l.u. in the two $Q$-space directions perpendicular to the $x$-axis in each case. (d) Markers show constant-energy cuts through the data shown in (a) and (b), averaged over 20–25 meV. Solid lines show the result of fitting Gaussians plus a flat background to the data. The gray diamonds in the (1 0 L) cut show the region of data excluded from the fit, as this region is dominated by the broad (001) type scattering from the (101) position.

Figure 8. (Color online) (a) and (b) Calculated spin wave dispersion of Mn$_{1+δ}$Sb along (H 0 2) and (1 0 L), respectively. The white circles are the points extracted from cuts through the data (see Fig. 7(d) and text) that were used to fit the model parameters. (c) Depiction of exchange constants used in the Heisenberg model, from 1st to 6th nearest neighbors for Mn1 ions.

Figure 9. (Color online) (a) and (b) Constant-energy cuts averaged over 20–25 meV from $E_i = 150$ meV SEQUOIA data measured at 10 K (circles), 200 K (triangles) and 443 K (diamonds). Cuts in (a) were averaged over ±0.1 r.l.u. in perpendicular $Q$-space directions, and successive cuts were offset 2 × 10$^{-4}$ for clarity. Cuts in (b) were averaged over ±0.2 r.l.u. in perpendicular $Q$-space directions. (c) shows the temperature dependence of the signal centered on (001), determined from (H01) cuts as described in the text. The plotted integrated intensity has been corrected for the Bose population factor.

unit of 3.2(1) $\mu_B$ at 10 K, taking into account the Mn2 occupancy of $\delta = 0.13(1)$, see Table I. The determination of a magnetic moment associated with the Mn2 site is further supported by the results from our DFT calculation. Previous modeling of Mn$_{1+δ}$Sb did not include an interstitial Mn, and those that attempted to account for it merely adjusted the electron count in stoichiometric MnSb models [5, 13, 21, 24, 42, 43]. We find a sizable moment on Mn2 in the calculation, see Fig. 4.

Given the presence of a magnetic moment on the interstitial site, in a simple local Heisenberg picture we would expect the antiparallel alignment of the interstitial to enhance the overall ferromagnetic state. However, it has clearly been observed that the presence of the interstitial acts to reduce $T_C$. [5, 8, 9]. Our DFT calculation shows that the interstitial Mn degrades the stability of the ferromagnetic state beyond the simple influence of changing lattice parameters (see Fig. 3), in agreement with the experimental observations. This indicates that a purely localized moment model may not be sufficient to describe the magnetic state in $\delta \neq 0$ Mn$_{1+δ}$Sb.

Our inelastic neutron scattering measurements of Mn$_{1+δ}$Sb serve to highlight the influence the intersti-
In addition to the spin wave, we identified a second magnetic signal in the spectrum which is broad in $Q$, and centered on an unexpected position in reciprocal space $Q = (001)$ (see Figs. 6, 7 and 9). Like the spin-wave scattering, this signal responds to $T_{SR}$, but unlike the spin-wave scattering, no similar signal is observed in interstitial-free MnBi. (001) is not an allowed nuclear or magnetic reflection (for either magnetic structure model discussed above). The presence of a (001) Bragg peak would require the correspondence between the upper and lower halves of the unit cell shown in Fig. 9(d) to be broken, for example, if Mn1 was antiferromagnetically aligned along c, or if Mn2 was only present in the lower half of the cell. However, we do not observe a Bragg peak at (001) in any of the neutron data sets collected, implying that no such long-range order is present.

Our results show that the inelastic signal at (001) is not associated with a long-range order in the system. The signal could, however, be associated with a short-range structural or magnetic order in the system. This proposition may be supported by the broad appearance of the signal in reciprocal space (see Fig. 9), which suggests a short correlation length in real space. We made a rough estimate for the correlation length by fitting Gaussians to cuts similar to those in Fig. 9(a) and (b), integrated over 10–15 meV, from the $E_i = 60$ meV, $T = 10$ K data. We find correlation lengths of ~16 Å in the $a$-$b$ plane, and in the range 10–18 Å along $c$ (where it is harder to define, due to the overlap of the signal with the spin-wave-type scattering), i.e. ~4 unit cells in plane, and ~3 units cells along $c$. We were unable to determine whether there is an elastic, diffuse scattering signal at the (001) position due to the neutron instrumentation used in this investigation. We do observe the signal down to the lowest energies that were probed on SEQUOIA, ~4 meV. A short range order could be present in the system if the interstitial Mn ions are not randomly distributed, but instead are structurally ordered over a few unit cells. Alternatively the presence of interstitials could modify the interactions of neighboring main-site Mn1 ions, with the associated magnetic excitations unable to propagate over large length scales due to disruption from a random distribution of magnetic Mn2 ions. Further studies, including diffuse neutron scattering experiments, are highly desirable to investigate the potential short-range order in this system.

The spectral weight of the (001) scattering, i.e. the total intensity of the signal integrated over $QE$ space, can in principal be used to indicate the strength of the magnetic excitations and therefore the size of the fluctuating magnetic moment, which could give an indication of the origin of the scattering. Unfortunately, due to the overlap of the two magnetic excitations in $QE$ space, we cannot quantitatively compare the spectral weights of the two signals. Qualitatively, however, by inspecting a series of slices and cuts through the data, such as those shown in Figs. 6, 7 and 9 we see that the strength of the signal emanating from (001) is comparable to the spin-wave signal. This implies that the (001) signal is associated with a relatively large magnetic moment per formula unit in the sample, of the order of the Mn1 moment size. This...
makes it unlikely to be purely the result of the Mn2 moments behaving independently of Mn1. Identification of the origin of this signal would be extremely significant for understanding the magnetic state in Mn_{1+δ}Sb and determining the possibilities of tuning the state with interstitial ions of Mn or other 3d transition metals.

**CONCLUSIONS**

We have shown that a magnetic moment on the interstitial Mn in Mn_{1+δ}Sb is required to describe the neutron diffraction data from a single crystal of Mn_{1+δ}Sb. This magnetic moment is aligned antiparallel to the main site Mn magnetic moment. We performed DFT calculations which find that the interstitial Mn is magnetic, consistent with the diffraction data. The DFT results are also consistent with previous experimental evidence that the interstitial reduces $T_C$ and $c$ lattice parameter, and increases $a$ in Mn_{1+δ}Sb. We find that the presence of the magnetic interstitial Mn also has a substantial effect on the magnetic excitation spectrum of Mn_{1+δ}Sb. It results in an apparent modification of the spin-wave spectrum, in addition to the appearance of an intense, broad signal, that cannot be explained by presently available tools for calculating magnetic dynamics.

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We employ the plane wave projector augmented wave (PAW) method [44] as implemented in the VASP code [45–47]. Atomic relaxations are converged down to 1 meV/Å. The number of plane waves is determined by an energy cut-off of 650 eV. For the Mn$_2$Sb$_2$, Mn$_4$Sb$_4$ and Mn$_9$Sb$_8$ unit cells a 8x8x5, 4x8x5 and 4x4x5 k-mesh is employed respectively. For the PBE+U calculations the double counting correction scheme by Dudarev et al. [48] is used. Atomic images were produced with the VESTA program [49].

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