Two dimensional ordering and collective magnetic excitations in the dilute ferromagnetic topological insulator (Bi$_{0.95}$Mn$_{0.05}$)$_2$Te$_3$

David Vaknin, Daniel M. Pajerowski, Deborah L. Schlagle, Kevin W. Dennis, and Robert J. McQueeney

1 Ames Laboratory, Ames, IA, 50011, USA
2 Department of Physics and Astronomy, Iowa State University, Ames, IA, 50011, USA
3 Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

Employing elastic and inelastic neutron scattering (INS) techniques, we report on detailed microscopic properties of the ferromagnetism in the magnetic topological insulator (Bi$_{0.95}$Mn$_{0.05}$)$_2$Te$_3$. Neutron diffraction of polycrystalline samples show the ferromagnetic (FM) ordering is long-range within the basal plane, and mainly 2D in character with short-range correlations between layers below $T_C \approx 13$ K. Despite the random distribution of the dilute Mn atoms, we find that the 2D-like magnetic peaks are commensurate with the chemical structure, and the absence of (00L) magnetic peaks denote that the Mn$^{2+}$ magnetic moments are normal to the basal planes. Surprisingly, we observed collective magnetic excitations, in this dilute magnetic system. Despite the dilute nature, the excitations are typical of quasi-2D FM systems, albeit are severely broadened at short wavelengths, likely due to the random spatial distribution of Mn atoms in the Bi planes. Detailed analysis of the INS provide energy scales of the exchange couplings and the single ion anisotropy.

Dilute magnetic systems, such as dilute magnetic semiconductors (DMS) or Kondo metals, are important materials that exploit the coupling of magnetism to charge carriers. Topological insulators (TI) are similar in that, time-reversal-symmetry-breaking by ferromagnetic (FM) ordering can gap the Dirac-like electronic states at the surface, and give rise to quantum anomalous Hall effect (QAHE) with chiral edge channels that can form dissipationless spin polarized currents[1]. To achieve that, dilute magnetic ions, such as Cr, V, or Mn, have been introduced into the tetradyminite TI systems, Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Sb$_2$Te$_3$ at the level of a few atomic percent resulting in long-range FM order with $T_C$ as high as 20 K [2-5]. Indeed, the QAHE has been observed in thin films of Bi$_2$Te$_3$ where bulk FM is induced by dilute substitutions with magnetic ions, such as Cr [6, 7] or V [8]. However, the QAHE is observed only at mK temperatures consistent with the FM ordering temperatures ($T_C < 20$ K).

To design materials that exhibit these phenomena at higher temperatures, it is imperative to understand the nature of bulk ferromagnetism in TIs, in particular, to determine the exchange interactions. The exchange interactions can be carried out by superexchange mechanism in insulating compounds, or by carrier-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange in metals and doped semiconductors. We note that FM-TIs share common features with DMS for which higher $T_C$’s have already been realized [9]. Like many DMS, such as Mn-doped GaAs, the location of solute atoms, substitutional or interstitial, and the role of solute clustering are important and sometimes raise controversial issues.

Here, we report on elastic and inelastic neutron scattering on prototypical dilute FM-TI (Bi$_{1-x}$Mn$_x$)$_2$Te$_3$.

Inelastic neutron scattering (INS) investigations are essential for determining the microscopic nature of the spatial and temporal correlations among magnetic ions. Our neutron diffraction data confirm homogeneous long-range FM ordering with short-range correlations between moment-bearing layers. The diluteness of FM-TI can make such measurements challenging, and INS measurements performed on DMS systems have not yielded deeper insight into collective magnetism [18]. Nonetheless, our INS measurements on polycrystalline samples of the dilute FM-TI (Bi$_{0.95}$Mn$_{0.05}$)$_2$Te$_3$ find evidence for long-range and quasi-two-dimensional (2D) ferromagnetism and gapped collective magnetic excitations in the FM ground state. Despite severe broadening of the dispersive features due to disorder, simple model calculations for a periodic triangular bilayer of local-moment magnetic ions capture the essential features of the INS data, providing key magnetic energy scales. Above $T_C$, persistent 2D spin correlations are observed with paramagnon character. These measurements provide unequivocal evidence of collective magnon excitations not yet observed in either DMS or FM-TI systems. At concentrations $x \leq 0.05$, Mn ions substitute randomly for Bi in the triangular layers of the tetradyminite structure and FM order sets in with $T_C$ up to 12 K has been reported [5, 10]. The characterization of bulk samples with $x < 0.05$ by magnetization, muon spin resonance, scanning probes [5, 10], and electron spin resonance (ESR) [11, 12] are all consistent with a homogeneous FM phase. For $x > 0.05$, a solubility limit is reached whereby Mn ions cluster and form heterogeneous Mn-rich regions [5, 10]. The RKKY mechanism is suggested by $p$-type metallic conductivity [5] and also first-principles calculations that find a weakly bound impurity band [13, 14]. Analysis of the critical fluctuations in the paramagnetic phase with ESR data are consistent with a long-range RKKY mechanism [11, 12]. Thus, a possible protocol to increase $T_C$ is to increase the impurity binding energy sufficiently to induce a metal-insulator transition [15, 16] which could deliver bulk insulating properties and high $T_C$, a desirable combination for QAHE [17].
The pure Bi$_2$Te$_3$ and doped (Bi$_{0.95}$Mn$_{0.05}$)$_2$Te$_3$ alloys were synthesized using high purity Bi 99.999% and Te 99.9999% (Alfa Aesar) and Mn 99.92% (distilled at Ames Laboratory). The metals were weighed out in the desired proportions and sealed in an 18 mm OD quartz tube under 15 Torr argon and baked in a box furnace at 750 C for 1 hour, and gently shaken twice during the dwell to ensure uniform mixing. After removing the sample from the furnace to air cool, the ingot was removed from the quartz and placed in a 20 mm OD carbonized Bridgman style quartz tube and sealed under 22 Torr argon. The quartz and ingot were placed in a Bridgman furnace with the bottom of the heat style quartz tube and sealed under 22 Torr argon. The sample was placed in a Bridgman furnace with the bottom taper of the quartz even with the bottom of the heat zone to ensure a temperature gradient was established across the ingot but the sample was not withdrawn following previously reported schedule[5].

We prepared 25 grams each of polycrystalline Bi$_2$Te$_3$ and (Bi$_{0.95}$Mn$_{0.05}$)$_2$Te$_3$. Electron energy dispersive spectroscopy measurements are consistent with the nominal Mn composition of $x \approx 0.05$. Curie-Weiss fits to the magnetic susceptibility measurements [Fig. 1(a)] confirm FM order with Weiss temperature $\theta = 13.5(1)$ K and an effective moment of $\mu_{eff} = 4.4(1)$ $\mu_B$ per Mn, consistent with previous reports [5, 10]. Magnetization measurements [inset of Fig. 1(a)] reveal a saturation moment of 4.4 $\mu_B$ per Mn at $T = 2$ K. For a successful INS observation of the weak magnetic signal from dilute Mn ions, it is critical to accurately subtract the signal due to phonon scattering. For this reason, we chose to study polycrystalline samples of the parent and doped compositions which have identical shapes that are fully illuminated by the neutron beam. A direct subtraction of the INS data measured on the parent compound from that of the Mn-doped composition, with no further corrections, provides an unambiguous signal from the magnetic fluctuations.

The elastic and inelastic neutron scattering experiments were conducted using the Cold Neutron Chopper Spectrometer (CNCS) [26, 27] at Oak Ridge National Laboratory. The polycrystalline samples (∼ 25 g) were sealed under helium in a cylindrical aluminum cans and mounted at the cold tip of a rod that was inserted in a liquid helium dewar (an ‘orange’ wet 4He cryostat). INS experiments were performed at the 2 – 20 K temperature range. The data were collected with the ‘high-flux-mode’ and fixed incident neutron energies of $E_i = 1.55$ meV, 3.32 meV, and 12.00 meV, which have approximately gaussian full-width-half-max instrumental resolutions at the elastic position of 0.04 meV, 0.11 meV, and 0.68 meV, respectively.

The MANTID software package [28] was used to reduce the time-of-flight data sets and to produce the scattering function $S(Q,E)$, where $Q$ is the magnitude of the momentum transfer and $E$ is the energy gain or loss of the neutron. Miller indices $(H,K,L)$ that are used throughout the manuscript to describe reciprocal space are defined with respect to the hexagonal axes. For further visualization, the DAVE software package was used [29].

The inset of Fig. 1(b) shows that the (101) diffraction peak intensity of the $x = 0.05$ sample at $T = 2$ K is enhanced relative to the 18 K peak due to FM ordering below $T_C$. The absence of magnetic intensity at (003) and (006) is evidence that the ordered moments have an easy-axis oriented perpendicular to the layers [5, 10], as shown in Fig. 1(d). Figure 1(b) shows the (101) diffraction signal at various temperatures minus the same scan taken at 18 K. The magnetic peak near (101) has an asymmetric Warren lineshape, which is commonly found in powder diffraction from 2-D crystalline systems [19]. Fits of the data to a Warren lineshape, as described in the Supplemental Material (SM)[30] and shown in Fig. 1(b), find a resolution limited correlation length ($\approx 300$ Å) within a layer, and a very short interlayer correlation length of only $\sim 7.5$ Å which confirms a strongly 2-D magnetic character. The integrated intensities of the (101) magnetic peaks as a function of temperature result in a mean-
dependence of the magnetic excitations through the cross-section and structural refinements of the elastic diffraction
describes in more detail the analysis of the magnetic diffraction
field-like squared order parameter, \( M^2 \propto (T_C - T) \), with
\( T_C = 13.3(2) \) K as shown in Fig. 2(c). The SM[30] de-
scribes in more detail the analysis of the magnetic diffrac-
T
non-magnetic Bi
Here
\( \chi \) imaginary part of the dynamical magnetic susceptibility,
\( S(Q,E) \) obtained for \((\text{Bi}_{0.95}\text{Mn}_{0.05})_2\text{Te}_3\) after subtracting the
\( S(Q,T) \) is
Debye-Waller factor (\( e^{-2W} \)) is one.

Figure 2(a) shows the dynamical susceptibility for
\((\text{Bi}_{0.95}\text{Mn}_{0.05})_2\text{Te}_3\) measured on CNCS with an incident
neutron energy of \( E_i = 3.32 \) meV and sample temper-
are generally too sharp, since dilution and dis-
order are not accounted for in our model.(see SM[30]).

\[
S(Q,E) \propto f^2(Q)e^{-2W}[1 + n(E)]\chi''(Q,E). \tag{1}
\]

Here \( n(E) \) is the Bose occupancy factor, \( f(Q) \) is the mag-
netic form factor for Mn\(^{3+}\). The dynamical susceptibil-
ity is extracted in arbitrary units after correcting for the
Bose and magnetic form factors. We assume that the
Debye-Waller factor (\( e^{-2W} \)) is one.

Data points overlayed on Fig. 2(a) are obtained from
fits to a series of constant-\( Q \) and constant-\( E \) cuts similar to those shown in Fig. 2(b), as described in the
SM[30]. These fits show a maximum magnon energy of
\( \hbar\omega_{\text{max}} \approx 2 - 2.5 \) meV and a dispersionless branch at
\( \hbar\omega_0 \approx 0.45 \) meV. As discussed below, the dispersionless
branch can be explained as an optical magnon branch,
or caused by localized magnetic excitations from isolated
Mn-Mn pairs. Figures 2(c) and 2(d) focus on lower en-
ergy excitations using \( E_i = 1.55 \) meV and \( T = 6 \) K.

The INS data suggest a minimal model for the spin dy-
namics. We assume that Mn ions occupy Bi sites and are
magnetically coupled within a bilayer of the quintuple-
layer structure, but with negligible coupling between the
bilayers [see Fig. 1(d)]. Despite the dilute and disordered
ature of the system, a periodic Heisenberg model with
nearest-neighbor (NN) coupling captures many of the
essential features of the data, as follows,

\[
H = -\langle J \rangle \sum_{\langle ij \rangle, A} S_{Ai} \cdot S_{Aj} - \langle J \rangle \sum_{\langle ij \rangle, B} S_{Bi} \cdot S_{Bj} - \langle J' \rangle \sum_{\langle ij \rangle, AB} S_{Ai} \cdot S_{Bj} - D \sum_i (S_i^\pm)^2. \tag{2}
\]

Here, \( A \) and \( B \) label two layers within the bilayer
that contain identical spins of magnitude \( S \), \( \langle J \rangle \) is the average
NN FM exchange within a single \( A \) or \( B \) layer, \( \langle J' \rangle \) is the average
NN FM exchange between \( A \) and \( B \) layers, and
\( D \) is the single-ion anisotropy.

Within linear spin wave theory of the Heisenberg
model (see SM[30]), the key energy scales are
\( \hbar\omega_{\text{max}} = 9S\langle J \rangle + 3S\langle J' \rangle \approx 2 \) meV, \( \hbar\omega_0 = \Delta + 6S\langle J' \rangle \approx 0.45 \) meV, and
\( \Delta = 2SD \approx 0.1 \) meV. From these relations,
we estimate that \( \langle J \rangle = 0.20 \) meV, \( \langle J' \rangle = 0.06 \) meV, and
\( SD = 0.05 \) meV. Using these values and assum-
ing \( S \approx 2 \), the mean-field Curie temperature, \( T_C = S(S+1)(6\langle J \rangle + 3\langle J' \rangle)/3k_B \approx 16 \) K, is in line with the
measured transition temperature. These energy scales
are also consistent with estimates based on ESR data,
although ESR measurements could not be performed in
the ordered state due to the spin gap [11, 12].

Using these exchange values, the dispersion and
the polycrystalline-averaged neutron scattering intens-
ities were calculated using Monte Carlo integration
methods[20]. While the general features of the INS
data are captured with this model, the calculated inten-
sities are generally too sharp, since dilution and dis-
order are accounted for in our model.(see SM[30]).
One expected consequence of disorder is the damping of magnons with wavelengths that are shorter than the mean spacing between NN moments. The convolution of these calculations with a phenomenological energy-dependent damping parameter \( \sigma_{\text{res}} = 0.045 \text{ meV} \) is the instrumental energy resolution and \( \beta = 0.28 \) improves the agreement.

As shown in Fig. 3, many qualitative features of the data are captured by the damped bilayer model. For example, comparison of Figs. 2(b) and 3(b) shows that the oscillation and width of constant-\( E \) \( Q \)-cuts are similar, but the energy dependence of the magnetic spectral weight is not. Finally, in the bilayer model, the localized mode at \( b \omega_0 \) can be interpreted as an optical magnon branch caused by opposite spin precession between the \( A \) and \( B \) layers. However, the localized mode is much sharper and stronger in the data which could indicate that it may alternatively be due to local spin dimer excitations from isolated Mn-Mn pairs. Similar spin dimer excitations have been observed in INS studies of DMS systems [18].

The spin fluctuations above \( T_C \) are characterized by relaxational dynamics typical of a nearly ordered FM system. Figure 4(a) shows the power spectrum \( \chi''(Q,E)/E \) of the excitations at \( T = 20 \text{ K} \). Figure 4(b) shows a gapless response and cuts at different \( Q \)-values are characterized by a relaxational (Lorentzian) form

\[
\frac{\chi''(Q,E)}{E} = \frac{\chi(Q) \Gamma(Q)}{E^2 + \Gamma(Q)^2}
\]

where \( \Gamma(Q) \) is the relaxation rate and \( \chi(Q) \) is the static susceptibility. Fitted values of \( \Gamma(Q) \), indicated by the white circles in Fig. 4(a), show a strong \( Q \)-dependence as expected for FM fluctuations (see SM[30]) [21]. The combined \( Q \)-dependences of \( \chi(Q) \) and \( \Gamma(Q) \) cause maxima in the paramagnetic response (black circles in Fig. 4(a)) commonly referred to as paramagnons. These features highlight that, both above and below \( T_C \), qualitative features of the magnetic excitations in \((\text{Bi}_{0.95}\text{Mn}_{0.05})_2\text{Te}_3\) are typical of a FM system despite the their dilute and disordered nature.

The microscopic nature of the magnetism in the dilute FM-TI \((\text{Bi}_{0.95}\text{Mn}_{0.05})_2\text{Te}_3\) has been revealed by INS. The FM order is long-range within the basal plane, but mainly 2D in character with short-range correlations between layers. The excitations are also typical of a quasi-2D FM system, despite the dilute distribution of Mn ions. Below \( T_C \), collective magnons are severely broadened at short wavelengths. We note that INS studies of DMS systems have shown localized excitations from Mn-Mn pairs, but have not yet revealed collective magnon modes[18]. This shows this our approach is a promising one for \((\text{Bi}_{1-x}\text{Mn}_x)_2\text{Te}_3\) and related dilute FM systems. In particular, methods developed in the DMS community to analyze magnetic excitations in dilute systems that serve to guide protocols to increase \( T_C \) [15, 16] can now be used for magnetic TIs.

In addition, our results also serve as tests of \textit{ab initio} theoretical calculations that provide a basis for estimating the strength of magnetic interactions in various dilute FM-TIs [14, 22–24]. With regard to Mn dopants,
all of these studies support hole-mediated RKKY-type exchange with predominantly FM interactions at short distances within a quintuple layer, consistent with our bilayer model analysis. More detailed first-principles estimates of the pairwise exchange interactions find both $J$ and $J'$ to be in the range from 2–4 meV with $J/J' \approx 1.5$ [22]. This is in reasonable agreement with our bilayer model where we estimate that $J \approx S(J)/xS = 2$ meV and $J' \approx S(J')/xS = 0.6$ meV, although the experimental value for $J'$ is subject to our interpretation that the dispersionless mode at 0.45 meV is an optical magnon branch. The prediction of a substantial FM coupling between bilayers Ref. [24] is not corroborated here. Our discovery that magnetism in (Bi$_{0.95}$Mn$_{0.05}$)$_2$Te$_3$ is strongly 2D is likely to carry over to other magnetic tetradymite systems and presents a hard limit for the highest achievable $T_c$.

Finally, with a promising basis for further INS measurements in hand, it will be illuminating to look for features in INS data that may arise from coupling of spin fluctuations to topologically protected charge carriers, especially with single-crystal samples. For example, ferromagnetic Weyl semimetals harbor chiral plasmons that are predicted to couple with magnons [25]. This will allow for signatures of topologically chiral electrons to be detected in the spin channel by INS.

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[30] See Supplemental Material at [URL will be inserted by publisher] on more detailed analysis of diffraction data and modeling the magnetic excitations.