PbCu$_3$TeO$_7$: an $S = \frac{1}{2}$ staircase kagome lattice with significant intra-plane and inter-plane couplings

B Koteswararao$^{1,2}$, R Kumar$^3$, Jayita Chakraborty$^4$, Byung-Gu Jeon$^2$, A V Mahajan$^3$, I Dasgupta$^4$, Kee Hoon Kim$^2$ and F C Chou$^{1,5}$

1 Center of Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan
2 CeNSCMR, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Republic of Korea
3 Department of Physics, Indian Institute of Technology Bombay, Mumbai 400076, India
4 Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India
5 National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

E-mail: fcchou@ntu.edu.tw

Received 31 May 2013, in final form 2 July 2013
Published 24 July 2013
Online at stacks.iop.org/JPhysCM/25/336003

Abstract

We have synthesized polycrystalline and single-crystal samples of PbCu$_3$TeO$_7$ and studied its properties via magnetic susceptibility, $\chi(T)$, and heat-capacity, $C_p(T)$, measurements and also electronic structure calculations. Whereas the crystal structure is suggestive of the presence of a quasi-2D network of Cu$^{2+}$ ($S = 1/2$) buckled staircase kagome layers, the $\chi(T)$ data show magnetic anisotropy and three magnetic anomalies at temperatures $T_{N1} \sim 36$ K, $T_{N2} \sim 25$ K, and $T_{N3} \sim 17$ K. The $\chi(T)$ data follow the Curie–Weiss law above 200 K and a Curie–Weiss temperature $\theta_{CW} \sim -150$ K is obtained. The data deviate from the simple Curie–Weiss law below 200 K, which is well above $T_{N1}$, suggesting the presence of competing magnetic interactions. The magnetic anomaly at $T_{N3}$ appears to be of first order from magnetization measurements, although our $C_p(T)$ results do not display any anomaly at $T_{N3}$. The hopping integrals obtained from our electronic structure calculations suggest the presence of significant intra-kagome (next-nearest neighbor and diagonal) and inter-kagome couplings. These couplings take the PbCu$_3$TeO$_7$ system away from a disordered ground state and lead to long-range order, in contrast to what might be expected for an ideal (isotropic) 2D kagome system.

(Some figures may appear in colour only in the online journal)

1. Introduction

Frustrated magnetism in kagome Heisenberg antiferromagnetic systems (KHAF) has been a major subject in condensed matter physics due to the unconventional, exotic ground states which emerge from the interplay between geometrical frustration and low dimensional quantum effects [1, 2]. In particular, quantum fluctuations for $S = 1/2$ systems are found to be strong among KHAF and can lead to interesting behavior like that of a spin liquid [3]. Theoretical studies on the ideal $S = 1/2$ isotropic KHAF lattice have demonstrated that it has a resonating valence bond (RVB)-like disordered ground state [4, 5]. Recent numerical studies [6] have also predicted that its ground state is a spin liquid with a small spin gap ($\Delta/k_B$) of (0.03–0.05)$J/k_B$ to its triplet excited state (where $J$ is the exchange interaction between nearest neighbor (nn) spins). A limited number of experimental realizations of structurally ideal, $S = 1/2$, KHAF have been found, which include Zn- and Mg-herbertsmithite, kapellasite, and haydeeite [7–9]. Among these, Zn-herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ is the best...
Figure 1. (a) The crystal structure of PbCu$_3$TeO$_7$ viewed along the $b$-direction is shown. (b) Projection of staircase (buckled) kagome planes in the $bc$-plane formed from Cu and O atoms with various bond angles [18]. The possible nearest neighbor (nn) exchange couplings between Cu1 and Cu2 atoms in the kagome layer are denoted by $J_1$, $J_2$, $J_3$, and $J_4$. The environments of the Cu1 octahedron, the Cu2 tetrahedron, and their coupling are shown in (c), (d), and (e). LDA calculations suggest various hopping paths for (f) intra-kagome plane and (g) inter-kagome planes indicated by $t_{in}$ and $t_{in}$, respectively.

example for explaining isotropic $S = 1/2$ KHAF behavior. Experimental studies on Zn-herbertsmithite have shown that there is no magnetic ordering down to $J/2k_B$ K, which implies that it has a disordered ground state [10]. But an unambiguous proof for the existence of a spin gap from an experimental point of view is lacking. The natural ion exchange of Cu and Zn or Mg is inevitable in these systems, which is probably the main obstacle to detecting the intrinsic nature of these $S = 1/2$ KHAF. On the other hand, there are a few anisotropic KHAF systems such as volborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O [11] and vesignieite BaCu$_3$V$_2$O$_8$(OH)$_2$ [12], which do not have much atomic site disorder, in which the kagome layers are built from two nearest neighbor (nn) exchange couplings.

These have also been studied in efforts to understand the real ground-state physics of a kagome system. Despite the presence of significant anisotropy, these systems show interesting spin dynamics [13]. There is another kind of anisotropic kagome lattice, in Rb$_2$Cu$_5$SnF$_{12}$ [14], where the kagome layer is formed from four exchange couplings and has a spin gap of 20 K. The pinwheel valence bond solid (VBS) excitations are realized in this anisotropic KHAF system [15].

Theoretical predictions also suggest that when the kagome layer is perturbed with additional exchange couplings such as next-nearest neighbor (nnn) and diagonal couplings, the system is driven to a novel ordered state from the disordered state of the isotropic kagome layer [16]. These predictions prompted us to look for newer $S = 1/2$, KHAF systems in order to explore interesting physics associated with the presence of anisotropy and additional couplings.

Herein, we introduce a new anisotropic magnetic system, PbCu$_3$TeO$_7$ [18], which has $S = 1/2$ staircase (buckled) kagome layers built from Cu and O atoms (see figure 1). This system has kagome layers similar to those of A$_3$V$_2$O$_8$ ($A = \beta$-Cu, Ni, Co) [19, 20]. Detailed studies have been done on single crystals of the $S = 1$ and $S = 3/2$ staircase kagome systems Ni$_3$V$_2$O$_8$ and Co$_3$V$_2$O$_8$. The Ni$_3$V$_2$O$_8$ system has four competing magnetic transitions (two incommensurate and two commensurate) below 9 K, one of which is a multiferroic transition at $T \sim 6$ K [21, 22]. However, Co$_3$V$_2$O$_8$ does not show multiferroicity, which might be due...
to its high spin state with low quantum fluctuations. Less work has been done on the $\delta = 1/2$ analog $\beta$-Cu$_3$V$_2$O$_8$, probably due to the lack of availability of single crystals.

We report here the magnetic properties of PbCu$_3$TeO$_7$. The magnetic susceptibility $\chi(T)$ data indicate that the dominant exchange interactions between Cu$^{2+}$ ions are antiferromagnetic (AF) with a Curie–Weiss temperature ($\theta_{CW}$) of about $-150 \, K$. The $\chi(T)$ deviates from Curie–Weiss behavior below $\sim 200 \, K$. We observed a total of three magnetic anomalies ($T_{N1} \sim 36 \, K$, $T_{N2} \sim 25 \, K$, and $T_{N3} \sim 16 \, K$) in the $\chi(T)$ data for a single crystal. The magnetic anomalies at $T_{N1}$ and $T_{N3}$ were evident only when the applied magnetic field $H$ was parallel to the crystallographic $a$-axis, whereas the one at $T_{N2}$ could be observed only for $H \parallel c$. The anomaly at $T_{N3}$ is first order in nature and is field sensitive. On the other hand, heat-capacity data in zero field (for both polycrystalline and single-crystal samples) showed anomalies of $T_{N1}$ and $T_{N2}$ only. The first-order transition at $T_{N3}$ could not be observed by us in heat-capacity data. We suggest that this might be due to the small latent heat involved in this transition. Our electronic structure calculations in conjunction with our experimental findings suggest the presence of various competing magnetic couplings, in addition to nn ones, in PbCu$_3$TeO$_7$ which in turn cause a deviation from the superficially anticipated regular kagome geometry leading to long-range order (LRO).

2. Experimental details

Polycrystalline samples of PbCu$_3$TeO$_7$ were prepared by the conventional solid-state reaction method using PbO, CuO, and Te precursors. The stoichiometric amounts of chemicals were ground thoroughly and fired at 750°C for five days with three intermediate grindings. To obtain single crystals, a mixture of PbCu$_3$TeO$_7$ and NaCl/KCl flux in the mass ratio 1:2 was charged in an alumina crucible, fired at 800°C from Quantum Design. For heat capacity, we employed using a Physical Property Measurement System (PPMS) performed on polycrystalline and single-crystal samples the crystals. Magnetic and heat-capacity measurements were collected using a D8 Advance (Bruker) for the single crystal flux with hot water. The x-ray diffraction (XRD) data were confirmed by comparing the measured XRD pattern with the calculated one generated by PowderCel [23] using the initial structural parameters of the orthorhombic space group Pnma (space group No. 62) given by Wedel et al [18]. Rietveld refinement of the XRD pattern was done using the Fullprof suite software [24] (as shown in figure 2(a)). The lattice parameters obtained from the refinement are $a = 10.484 \, \text{Å}$, $b = 6.347 \, \text{Å}$, and $c = 8.807 \, \text{Å}$. The atomic positions and occupancies obtained are summarized in table 1. These structural parameters are in good agreement with the previously published values [18]. A rectangular crystal was placed on a glass slide with the top face (see figure 2) parallel to the plane of the slide and XRD was performed. It resulted in the appearance of only $(00l)$ peaks as shown in figure 2(b). This indicates that the top crystal surface (as indicated in

3. Results and discussion

3.1. X-ray diffraction and structural features

The single-phase nature of the polycrystalline sample was confirmed by comparing the measured XRD pattern with the calculated one generated by PowderCel [23] using the initial structural parameters of the orthorhombic space group Pnma (space group No. 62) given by Wedel et al [18]. Rietveld refinement of the XRD pattern was done using the Fullprof suite software [24] (as shown in figure 2(a)). The lattice parameters obtained from the refinement are $a = 10.484 \, \text{Å}$, $b = 6.347 \, \text{Å}$, and $c = 8.807 \, \text{Å}$. The atomic positions and occupancies obtained are summarized in table 1. These structural parameters are in good agreement with the previously published values [18]. A rectangular crystal was placed on a glass slide with the top face (see figure 2) parallel to the plane of the slide and XRD was performed. It resulted in the appearance of only $(00l)$ peaks as shown in figure 2(b). This indicates that the top crystal surface (as indicated in

![Figure 2.](image-url)
anisotropy (the difference between the [0ll] direction or bc-plane. This means that the a-axis lies in the as-grown plane of the crystal. Note that crystallographic a-axis is perpendicular to the staircase kagome layers, as shown in figure 1(b). We have further taken the Laue pattern of the crystal, and found that the crystallographic a-axis is along the length of the crystal. The other crystallographic axes (b and c) were also identified and make roughly 45° with the top plane of the crystal, as shown in the inset of figure 2(b).

The staircase kagome planes in the PbCu₃TeO₇ [18] structure are formed from Cu atoms (Cu1 and Cu2) as shown in figure 1. The Cu²⁺ ions are coupled via O²⁻ ions and form buckled layers in the bc-planes, as shown in figure 1(b). According to the Cu–Cu bond lengths and the Cu–O–Cu bond angles, the staircase kagome plane possibly has four different nearest neighbor (nn) exchange constants J₁, J₂, J₃ and J₄ (see figure 1(b)). In this staircase kagome plane, Cu1 atoms form linear chains with the couplings alternating between J₂ and J₄. These Cu1 chains are connected with each other via Cu2 atoms with couplings J₁ and J₃ to form a 2D network. Other possible magnetic coupling paths are also shown in figure 1(f), the hopping integrals for which have been calculated by us. These are t₅, t₆, t₇, and t₈ which are in addition to the nn hoppings t₁, t₂, t₃ and t₄ (corresponding to J₁, J₂, J₃ and J₄, respectively). The kagome planes are separated by Pb and Te atoms with a small inter-planar distance of about 4 Å, which suggests that significant three-dimensional couplings between the layers might be present.

3.2. Magnetic measurements

The magnetization M was measured as a function of temperature T. The dependences of the magnetic susceptibility \( \chi (=M/H) \) in the range from 2 to 370 K for the polycrystalline and single-crystal samples of PbCu₃TeO₇ are shown in figure 3(a). Magnetic measurements were performed on the 2 mg single crystal (shown in figure 2(b)) for each of the crystal directions a, b, and c, respectively in an applied magnetic field H. The \( \chi(T) \) data follow a Curie–Weiss behavior in the high T region. Even in the paramagnetic region, a significant anisotropy is seen between the field orientation along a and the other two perpendicular directions (b and c). This means that the intra-kagome (bc-plane) anisotropy (the difference between the b- and c-axis) is small compared to the inter-kagome anisotropy. The \( \chi(T) \) data for the polycrystalline sample lie in between the single-crystal data for \( H \parallel a \) and \( H \parallel bc \), but for \( T > 200 \) K they are close to the single-crystal data for \( H \parallel a \), while below 200 K they are closer to the single-crystal data for \( H \perp a \). The temperature-independent magnetic susceptibility \( \chi₀ \) was estimated from polycrystalline data at high T from 300 to 800 K (data not shown here). We subtracted \( \chi₀ = -(3 \pm 0.3) \times 10^{-5} \) cm³/mol Cu from our measured data.
Curie–Weiss (CW) law with those for other cuprates [26]. The \( \chi(\mathbf{H}) \) susceptibility is then estimated to be \( -\chi_0 / T \) with \( \chi_0 \) calculated to be \( -\chi_0 / T \) cm\(^{-3}\) mol\(^{-1}\) Cu, which is comparable to other cuprates [26]. The Van Vleck paramagnetic susceptibility is then estimated to be \( \chi_{VV} = \chi_0 - \chi_{core} \sim (2.23 \pm 0.3) \times 10^{-5} \) cm\(^{-3}\) mol\(^{-1}\) Cu, which is comparable with those for other cuprates [26]. The \( \chi(T) \) data follow the Curie–Weiss (CW) law \( \frac{C}{T} = \frac{\chi_{CW}}{T} \) in the \( T \)-range 200–370 K where \( C \) is the Curie constant and \( \theta_{CW} \) is the Curie–Weiss temperature. The parameters obtained from the single-crystal data are given in table 2. The \( C \) value corresponds to an effective magnetic moment \( \mu_{eff} = \frac{C}{\theta_{CW}} \) of about 2 \( \mu_B \) Cu, which is slightly larger than the spin-only value for \( S = 1/2 \) which is 1.73 \( \mu_B \). The negative \( \theta_{CW} \) indicates that the dominating couplings are antiferromagnetic in nature. There is a deviation from the Curie–Weiss law below 200 K, which indicates that it is not a simple paramagnet at low \( T \). This deviation might be a result of the competitive exchange couplings present in the quasi-2D staircase kagome planes. The \( \chi(T) \) data for polycrystalline samples exhibit a total of three magnetic anomalies at \( T_{N1} \sim 36 \) K, \( T_{N2} \sim 25 \) K, and \( T_{N3} \sim 17 \) K. The ordering temperature \( (T_{N1}) \) is smaller than \( \theta_{CW} \) and the temperature below which a deviation from CW behavior is seen (200 K), which indicates that the system is moderately frustrated. These three magnetic anomalies \( (T_{N1}, T_{N2} \) and \( T_{N3}) \) are also seen in the single-crystal data, but with significant anisotropy. All of the anomalies are not evident for each field direction. For instance, the magnetic anomaly \( T_{N1} \) is evident only when \( H \parallel a \), and the anomaly at \( T_{N2} \) is seen only for \( H \parallel b \). On the other hand, for \( H \parallel c \), no clear anomalies were observed. The anomaly at \( T_{N3} \) is prominent for \( H \parallel a \) (see figure 4). Although the appearance of anomalies in the \( \chi(T) \) data depends on the field direction, the transitions are not field driven because the two anomalies \( (T_{N1} \) and \( T_{N2}) \) appear in zero-field heat-capacity data as will be discussed in a later section. Similar \( H \)-direction-dependent anomalies were also reported for a multiferroic, spiral magnet FeVO\(_4\) [27]. The susceptibility \( \chi_b \) \( \chi(T) \) for \( H \parallel b \) increases below the transition while \( \chi_a \) and \( \chi_c \) decrease below the transition. This suggests that the \( b \)-axis might be the hard axis of magnetization.

In order to obtain insight about the transition at \( T_{N3} \), we have measured \( M \) for a collection of carefully oriented crystals \( (H \parallel a) \), while cooling and warming in different fields \( H \) of 1 kOe, 5 kOe, 10 kOe, 15 kOe, respectively, as shown in figure 4. The transition at \( T_{N3} \) is sharp and looks different from those at \( T_{N1} \) and \( T_{N2} \). There is a difference in the position of the peak for the zero-field-cooled warming

![Graph showing magnetic susceptibility data](image)

**Figure 4.** The magnetic susceptibility of \( \text{PbCu}_5\text{TeO}_7 \) in the orientation \( H \parallel a \) for different magnetic fields (a) 1 kOe, (b) 5 kOe, (c) 10 kOe and (d) 15 kOe is plotted. The black solid line indicates zero-field-cooled (ZFC) warming data, while the red and blue solid lines are the data related to field-cooled (FC) cooling and FC warming, respectively. The red and black arrow marks indicate the positions of the magnetic anomaly in the cooling and warming data, respectively. Both warming and cooling data were collected by sweeping the temperature with a rate of 1 K min\(^{-1}\).

| Table 2. The parameters obtained from the Curie–Weiss fit in the temperature range from 200 to 370 K. |
|---|---|---|---|
| \( T \)-range (K) | \( C \) (cm\(^3\) K/mol Cu) | \( \theta_{CW} \) (K) | \( \mu_{eff} \) (\( \mu_B \)) |
| \( H \parallel a \) 200–370 | 0.52 \( \pm \) 0.05 | \( -145 \) \( \pm \) 5 | 2.04 |
| \( H \parallel b \) 200–370 | 0.49 \( \pm \) 0.05 | \( -155 \) \( \pm \) 5 | 1.98 |
| \( H \parallel c \) 200–370 | 0.46 \( \pm \) 0.05 | \( -140 \) \( \pm \) 5 | 1.92 |
Table 3. The variation of magnetic peak positions of $T_{N3}$ in the cooling and warming $M(T)$ data in different magnetic fields.

| $H$ (kOe) | $T_{N3}$ (K) (FC cooling) | $T_{N3}$ (K) (ZFC warming) | Difference $\Delta T$ (K) |
|-----------|---------------------------|-----------------------------|--------------------------|
| 1         | 15.8 ± 0.1                | 16.5 ± 0.1                  | 0.7                      |
| 5         | 16.3 ± 0.1                | 16.8 ± 0.1                  | 0.5                      |
| 10        | 17.2 ± 0.1                | 17.5 ± 0.1                  | 0.3                      |
| 15        | 17.5 ± 0.1                | 17.7 ± 0.1                  | 0.2                      |

(ZFCW) data and the field-cooled cooling (FCC) data, while no difference is observed between ZFC warming and FC warming (FCW) data. This kind of thermal hysteresis is a characteristic feature of a first-order phase transition [28]. Similar sharp, first-order anomalies are also observed at 3.9 K in Ni$_2$V$_2$O$_6$ [21] and 6 K in Co$_3$V$_2$O$_8$ [30] staircase kagome systems. Moreover, the observed peak position moves to higher temperatures with increasing $H$ and this variation (summarized in table 3) suggests that the observed first-order transition is ferromagnetic in nature. The $T_{N3}$ peak also broadens and the difference between the positions (in temperature) of the warming and cooling peak decreases as $H$ increases. This kind of field-induced broadening is also a characteristic feature of the first-order transition [29]. Finally, the $T_{N3}$ peak is suppressed in a field of about 20 kOe; however the $T_{N1}$ and $T_{N2}$ peaks remain, more or less, unaffected by magnetic fields up to 70 kOe and do not exhibit any thermal hysteresis like that observed for $T_{N3}$ (data not shown here).

3.3. Heat-capacity measurements

The $T$-dependent heat capacity $C_p$ of the polycrystalline PbCu$_2$TeO$_7$ samples in the range from 2 to 300 K is presented in figure 5. The $C_p(T)$ data were measured using the PPMS by the thermal relaxation method. For a magnetic insulator, one expects both lattice and magnetic contributions to the heat capacity. We, first, used a single Debye integral [31] to fit the data, but this did not result in satisfactory fits. With atoms of different masses in the unit cell, it is possible that different normal modes involve different atoms and might have differing Debye temperatures. We were then able to fit the data to the following formula, which contains a linear combination of two Debye integrals, for the $T$-range from 150 to 300 K:

$$C_p(T) = 9rNk_B \sum_{i=1,2} C_i \left( \frac{T}{\theta_D^i} \right)^3 \int_0^{\theta_D^i} \frac{x^4 e^x}{(e^x - 1)^2} \, dx.$$

(1)

Here $r$ is the number of atoms per formula unit, $\theta_D^i$ is a Debye temperature, and $x_D = \theta_D^i/T$ ($i = 1, 2$). The fitting yields $C_1 = 0.43 \pm 0.05$, $\theta_D^1 = 280 \pm 10$ K, $C_2 = 0.5 \pm 0.05$, and $\theta_D^2 = 772 \pm 30$ K. The fitting curve was extrapolated down to 2 K and this was then subtracted from the measured $C_p(T)$. The magnetic heat capacity $C_m(T)$ was thus obtained (see the inset of figure 5). Sharp anomalies are observed at 36 and 25 K, which agree well with the anomalies found at $T_{N1}$ and $T_{N2}$ in $\chi(T)$. We observed the presence of $C_m(T)$ up to 150 K which is well above $T_{N1}$. Please note that more than 98% of $C_m$ is recovered below 100 K. This signifies the presence of magnetic correlations above $T_{N1}$ and this behavior is also consistent with the magnetic data. However, we could not detect any transition at $T_{N3}$ in the data. In fact, detailed $C_p(T)$ measurements were done around 16 K with a large number of points. The raw data for the sample temperature as a function of time at each of these temperatures showed a good fit to the $2\tau$ model. In the case of a first-order transition, it has been documented that deviations from the simple $2\tau$ behavior occur for $C_p$ data at the transition temperature [32]. In light of the lack of supporting evidence for $T_{N3}$ from the $C_p(T)$ measurement, one may suspect that the existence of $T_{N3}$, from susceptibility data, may not be intrinsic. On the other hand, the inability to detect a similar kind of first-order phase transition has also been argued in the literature [32]. Some other technique like the adiabatic method or a better pulse-sequence design [33] may be needed for measuring small latent heat or entropy change transitions. Although our heat-capacity measurements do not support the existence of the $T_{N3}$ phase transition, we must stress that the $T_{N3}$ anomaly has been consistently observed in the magnetization measurements for different batches of powder samples as well as single crystals, i.e., the possibility of a contribution from an external magnetic impurity phase due to different preparation conditions or contamination can be ruled out. More sensitive heat-capacity measurements are being planned, to clarify this issue. Overall we conclude that the intrinsic origin of this transition is an open question.

The entropy change $S_m$ per Cu calculated from magnetic heat capacity is about 5.63 J K$^{-1}$ mol$^{-1}$, which is in good
agreement with the expected $R \ln (2S + 1)$ (5.76 J K$^{-1}$ mol$^{-1}$) for $S = \frac{1}{2}$ systems. The $S_m$ value per Cu at transition $T_{N1}$ is found to be 2.88 J K$^{-1}$ mol$^{-1}$, which is 50% of the total entropy, and the rest of the entropy is released in the paramagnetic region well above $T_{N1}$, suggesting the presence of frustrated or short-range correlations. The observation of significant entropy well above the ordering temperature is generally observed in frustrated spin systems [34]. Additionally, nearly all the entropy change has taken place by the time one approaches (with decreasing temperature) the $T_{N3}$ transition.

### 3.4. Electronic structure calculations

In order to study the electronic structure of PbCu$_3$TeO$_7$, we have carried out first-principles density functional theory (DFT) calculations within the local-density approximation (LDA) by employing the Stuttgart TB-LMTO-47 code based on the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) [35]. The basis set for the self-consistent electronic structure calculations for PbCu$_3$TeO$_7$ in the TB-LMTO ASA includes Pb (s, p), Cu (s, p, d), Te (s, p) and O (s, p) and the rest are downfolded. A (4, 8, 4) $k$-mesh has been used for self-consistency. All the $k$-space integrations were performed using the tetrahedron method. In order to ascertain the accuracy of our ASA calculations we also performed the electronic structure calculation using the projected augmented wave (PAW) [36] method encoded in the Vienna ab initio simulation package (VASP) [37]. The densities of states calculated by these two different approaches are found to agree well with each other. In order to extract various integrals of hopping between the Cu atoms, we have employed the $N^\text{th}$-order muffin-tin orbital (NMTO) downfolding method [38–40].

The non-spin-polarized band structure for PbCu$_3$TeO$_7$ is displayed in figure 6. The bands are plotted at the various high symmetry points of the Brillouin zone corresponding to the orthorhombic lattice. All the energies are measured with respect to the Fermi level of the compound. The characteristic feature of the non-spin-polarized band structure displayed in figure 6 is an isolated set of twelve bands crossing the Fermi level and these bands are predominantly derived from the antibonding linear combination of Cu d$_{x^2-y^2}$ and O p states. These twelve bands are well separated from the low-lying O p and other Cu d valence bands. This isolated Cu d$_{x^2-y^2}$ twelve-band complex is responsible for the low energy physics of this compound.

Figure 6. Downfolded band structure (shown in red lines) compared to the full orbital band structure (shown in black lines) for PbCu$_3$TeO$_7$.

Figure 7. Partial density of states obtained from LMTO-ASA.
Cu1 octahedron forming a strong pdσ antibond with the Cu1 d_{2z²−y²} orbital. The nn hopping t₁ between the edge sharing Cu1 octahedron (see figure 1(c)) and Cu2 tetrahedron (see figure 1(d)) is found to be much smaller than t₃. In order to obtain further insights, we have plotted the Wannier function of the Cu2 d_{2z²−y²} orbital corresponding to the t₃ and t₁ hoppings (see figure 8). The plot reveals that the Cu2 d_{2z²−y²} orbital forms strong pdσ antibonds with the neighboring oxygens. We can see that the weight of the Wannier function at Cu1 site which is at a distance 3.264 Å is large compared to the weight at the Cu1 site which is at a distance 2.90 Å, indicating that t₃ hopping will be stronger in comparison to t₁ hopping. The bond angle of Cu1−O2−Cu2 corresponding to the t₃ hopping is 118.06°, while the bond angle of Cu1−O1−Cu2 is 93° for the t₁ hopping path. The strengths of antiferromagnetic interactions are strongly dependent on the angle between the bonds. When the angle is close to 90°, the AF super-exchange process is suppressed due to the orthogonality of Cu 3d and O 2p orbitals. So the exchange coupling along the path t₁ is expected to be ferromagnetic. For t₄ hopping, two Cu1 octahedra are corner shared with each other and the bond angle of Cu1−O3−Cu1 is 107°, while for the t₂ hopping path, the two Cu1 octahedra share an edge with each other and the bond angle of Cu1−O2−Cu1 is 105°. As argued earlier, the t₃ hopping dominates over the t₂ hopping path due to the corner sharing topology of the Cu1 octahedra. The second strongest hopping is t₁ between the Cu2 atoms. This Cu2−Cu2 hopping primarily proceeds via the oxygens. As a result, the strength of the Cu−O4−O4−Cu spin exchange is primarily governed by the O−O distance and in this case the O−O distance is 2.57 Å (smaller than the van der Waals distance). Moreover, the bond angle of Cu−O4−O4 is about 167°, which makes this hopping stronger than some of the nn hoppings (t₂, t₃, and t₄).

The hopping paths perpendicular to the kagome plane are listed in table 5. Since the distances between the Cu ions in two different kagome planes are small, there is expected to be a substantial amount of hopping between the kagome planes. The strongest interaction between the kagome planes is t₂. This interaction is mediated via Te following the path Cu−O−Te−O−Cu.

Our electronic structure calculations reveal that intra-kagome and inter-kagome exchange interactions are long ranged. In general, an ideal 2D kagome system with only uniform nn couplings does not order even at zero T. However, spin wave theory [16] predicts that the presence of second-nn (J_{nnn}) and third-nn (J_{diagonal}) couplings in the kagome plane can drive the system to an ordered ground state. When J_{diagonal} > J_{nnn}, a √3×√3 Néel ordered state is favored, while the q = 0 Néel state occurs in the case of J_{nnn} > J_{diagonal}. A rich theoretical magnetic phase diagram has also been built on the basis of the type (antiferromagnetic or ferromagnetic) and the relative strength (J_{nnn}/J_{diagonal}) of the interactions in the 2D kagome system [9, 17]. Since the kagome planes

Table 4. Hopping (in meV) between various Cu atoms within the kagome plane, obtained from the NMTO downfolding method.

| Coupling between | Hopping path | Distance (Å) | Hopping (meV) | Bond angle and bond lengths |
|------------------|--------------|--------------|---------------|-----------------------------|
| Cu1−Cu2 (nn)    | t₁           | 2.90         | 46.23         | Cu1−O4−Cu2 ~ 92.9°, Cu1−O1−Cu2 ~ 83.1° |
| Cu1−Cu1 (nn)    | t₂           | 3.065        | 42.17         | Cu1−O2−Cu1 ~ 105°         |
| Cu1−Cu2 (nn)    | t₃           | 3.264        | 149.67        | Cu1−O2−Cu2 ~ 118.1°       |
| Cu1−Cu1 (nn)    | t₄           | 3.29         | 91.16         | Cu1−O3−Cu1 ~ 107.6°, Cu1−O1−Cu2 ~ 91° |
| Cu2−Cu2 (nnn)   | t₅           | 5.43         | 57            | O1−O4 ~ 2.8 Å, Cu2−O1−O4 ~ 152°, O1−O4−Cu2− ~ 110° |
| Cu1−Cu2 (nnn)   | t₆           | 5.617        | 19.05         | O1−O5 ~ 2.78 Å            |
| Cu2−Cu2 (diagonal) | t₇         | 6.353        | 104.76        | O4−O4 ~ 2.57 Å, Cu2−O4−O4 ~ 167°, O4−O4−Cu2 ~ 167° |
| Cu1−Cu2 (long range) | t₈       | 6.7          | 49            | O−O ~ 2.83 Å             |

Table 5. Hopping parameters (in meV) for the inter-kagome plane, obtained from the NMTO downfolding method.

| Coupling between | Hopping path | Distance (Å) | Hopping (meV) | Bond angle and bond lengths |
|------------------|--------------|--------------|---------------|-----------------------------|
| Cu2−Cu2          | t₁           | 5.92         | 16.32         | Cu1−O3−Te−O4−Cu2, O3−O4 ~ 2.72 Å |
| Cu1−Cu2          | t₂           | 6.12         | 49            |                             |
| Cu1−Cu2          | t₃           | 6.27         | 20.41         |                             |
| Cu2−Cu2          | t₄           | 6.27         | 28.53         |                             |

Figure 8. Wannier function of Cu d_{2z²−y²} placed at the Cu2 site.
of PbCu$_3$TeO$_7$ appear to have additional couplings (second and third nn), they might support ordered magnetic states as mentioned above. In addition, there are also substantial inter-planar couplings found in this system. These additional intra-kagome and inter-kagome couplings might be the reason for having different AF transitions in this system. Detailed neutron diffraction measurements and analysis will however be needed to clarify the origin and nature of these transitions.

4. Conclusions

On the basis of the structural details, one forms the impression that PbCu$_3$TeO$_7$ might have quasi-2D staircase (buckled) kagome layers. However, our magnetic measurements on polycrystalline and single-crystal samples show the onset of LRO at around 36 K with a change in the spin order around 25 K. This indicates the existence of significant three-dimensional couplings. $\chi(T)$ is found to obey the simple Curie–Weiss law above 200 K with a Curie constant as expected for a paramagnetic system. However, below 200 K there is a deviation from the Curie–Weiss behavior, though it is well above $T_N$, which suggests the presence of frustrated or short-range spin correlations well above $T_N$. This behavior is also consistent with $C_p(T)$ which implies the presence of magnetic entropy well above the magnetic transitions. We performed electronic structure calculations to determine the relative values and importance of the various exchange paths. Our results suggest the presence of various intra-kagome (nn and diagonal) and inter-kagome exchange hopping paths, which then must be responsible for the onset of LRO in this system. Detailed neutron diffraction measurements will be helpful for understanding more about the nature of the spin orderings and magnetic phase diagram of this system.

Acknowledgments

The authors FCC and BKR acknowledge the support from the National Science Council of Taiwan under project number NSC 101-2119-M-002-007. JC thanks CSIR India (Grant No. 90/080(0615)/2008-EMR-1) for a research fellowship. AVM and RK thank the Department of Science and Technology and CSIR, India, for financial support. The work at SNU was supported by the National Creative Research Initiative (2010-0018300).

References

[1] Misguich G and Lhuillier C 2005 Frustrated Spin Systems ed H T Diep (Singapore: World Scientific)
[2] Lacroix C, Mendels P and Mila F 2010 Introduction to Frustrated Magnetism (Berlin: Springer)
[3] Balents L 2010 Nature 464 199
[4] Sachdev S 1992 Phys. Rev. B 45 12377
[5] Chalker J T and Eastmond J P G 1992 Phys. Rev. B 46 14201
[6] Yan S, Huse D A and White S R 2011 Science 332 1173
[7] Shores M P, Nytko E A, Bartlett B M and Nocera D G 2005 J. Am. Chem. Soc. 127 13462
[8] Helton J S et al 2007 Phys. Rev. Lett. 98 107204
[9] Janson O, Richter J and Rosner H 2008 Phys. Rev. Lett. 101 164003
[10] Fäk B et al 2012 Phys. Rev. Lett. 109 037208
[11] Mendels P et al 2007 Phys. Rev. Lett. 98 077204
[12] Lafontaine M A, Bail A L and Férey G 1990 J. Solid State Chem. 85 220
[13] Okamoto Y, Yoshida H and Hiroi Z 2009 J. Phys. Soc. Japan 78 033701
[14] Colman R H, Bert F, Boldrin D, Hillonier A D, Manuel P, Mendels P and Wills A S 2011 Phys. Rev. B 83 180416
[15] Morita K, Yano M, Ono T, Tanaka H, Fujii K, Uekusa H, Harumi Y and Kindo K 2008 J. Phys. Soc. Japan 77 043707
[16] Matan K, Ono T, Fukumoto Y, Sato T J, Yamamura J, Yano M, Morita K and Tanaka H 2010 Nature Phys. 6 865
[17] Harris A B, Kallin C and Berlinsky A J 1992 Phys. Rev. B 45 2899
[18] Demenge J-C, Sindzingre P, Lhuillier C and Pierre L 2005 Phys. Rev. B 72 024433
[19] Wedel B and Mueller-Buschbaum H 1996 Z. Naturf. B 51 1587
[20] Rogado N, Haas M K, Lawes G, Huse D A, Ramirez A P and Cava R J 2003 J. Phys.: Condens. Matter 15 907
[21] Rogado N, Lawes G, Huse D A, Ramirez A P and Cava R J 2002 Solid State Commun. 124 229
[22] Lawes G et al 2004 Phys. Rev. Lett. 93 247201
[23] Lawes G et al 2005 Phys. Rev. Lett. 95 087205
[24] Motoyama N, Eisaki H and Uchida S 1996 Phys. Rev. Lett. 76 3212
[25] Daoud-Adaline A, Kundys B, Martin C, Radaelli P G, Brown P J, Simon C and Chapon L C 2009 Phys. Rev. B 80 220402
[26] Nirmala R, Mudryk Ya, Pecharsky V K and Gschneidner Jr K A 2007 Phys. Rev. B 76 104417
[27] Rojas D P, Espeso J I, Rodriguez-Fernandez J, Gomez Sal J C, Sanchez Marcos J and Muller H 2009 Phys. Rev. B 80 184413
[28] Rojas D P, Espeso J I, Rodriguez-Fernandez J, Gomez Sal J C, Rusu C, Andreica D, Dudric R and Amato A 2011 Phys. Rev. B 84 024403
[29] Chen Y et al 2006 Phys. Rev. B 74 014430
[30] Yasui Y, Kobayashi Y, Soda M, Moyoshi T, Sato M, Igawa N and Kakurai K 2007 J. Phys. Soc. Japan 76 034706
[31] Kittel C 1996 Introduction to Solid State Physics (Wiley)
[32] Lashley J C et al 2003 Cryogenics 43 369
[33] Suzuki H, Inaba A and Meingast C 2010 Cryogenics 50 693
[34] Newsome R W Jr and Andrei E Y 2004 Rev. Sci. Instrum. 75 104
[35] Alexander L K, Bütgen N, Nath R, Mahajan A V and Loidl A 2007 Phys. Rev. B 76 064429
[36] Andersen O K and Saha-Dasgupta T 2000 Phys. Rev. B 62 R16219
[37] Andersen O K, Saha-Dasgupta T, Tank R W, Arcangel C, Jepsen O and Krier G 2000 Springer Lecture Notes in Physics vol 535 (Berlin: Springer) pp 3–84
[38] Andersen O K, Saha-Dasgupta T and Ezhev S 2003 Bull. Mater. Sci. 26 19