Chapter 5

CuCrSe$_2$: Electronic Transport and Magnetic Properties

Abstract

In this chapter we present a detailed study of electronic transport (Electrical resistivity, Hall effect and thermoelectric power) and magnetic properties (magnetic susceptibility and magnetization) of CuCrSe$_2$ from 2 K-300 K. We also present a comparative study of heat capacities $C_P$ of CuCrS$_2$ and CuCrSe$_2$. The electrical resistivity shows metallic behavior down to 2 K. The thermoelectric power is large 100$\mu$VK$^{-1}$ at 300 K. Weak anomalies in resistivity and a rounded maximum in $\chi$ are observed around 55 K. A sharp transition, as expected for 3-dimensional magnetic order, absent in the heat capacity of CuCrSe$_2$, rather a visible maximum is observed at 55 K. At low temperatures between 2 K to 14 K, the magnetic heat capacity $C_{mag}$ follows $T^2$-dependence. We explain this behavior as a result of the suppression of magnetic order in CuCrSe$_2$ due to competing magnetic interactions between intra and inter layer Cr atoms. The ferromagnetic indirect exchange among intra-layer Cr atoms increases in the more metallic selenide compound, and competes with direct antiferromagnetic interactions between the interlayer Cr atoms leading to destruction of long range magnetic order.
5.1 Introduction

In ABX$_2$(A=Li, Na, K, Cu or Ag, B=Fe, Cr or Al and X=O, S or Se) magnetic Fe and Cr atoms form a triangular lattice antiferromagnet (TLA) system. The strong geometrical frustration of spins in them results in absence of magnetic order and at low temperature exotic magnetic, magnetostrictive and magnetoelastic properties are observed. Among them the oxides (CuFeO$_2$, CuAlO$_2$ and CuCrO$_2$) form in the delafossite structure and show multiferroic properties [1]. In CuCrO$_2$ spin driven ferroelectricity has recently been discovered in the magnetic ground state [2].

The corresponding sulfide and selenide compounds of Cr, ACrX$_2$(A=Li, Na, K, Cu or Ag; X=S, Se) on the other hand show antiferromagnetic ordering at low temperatures between 19 K to 55 K [3-7]. Recently, neutron diffraction studies have been done to understand the non-collinear magnetic ordering and the associated magneto-elastic properties of Cu(Ag)CrS$_2$ using a model of geometrical frustration (Heisenberg antiferromagnet on a triangular lattice (HAFT)) that is applicable in case of delafossite oxides discussed above. These studies clearly evidenced a magnetoelastic-coupling induced structural phase transition into a monoclinic phase at $T_N$ [8, 9].

The magnetic interactions among intra-layer Cr atoms, the dependence of Cr-Cr separation and the observed helical order at low temperatures in these chalcogenide compounds of Cr has been discussed in detail in Chapter(1) section(1.3). It is however, not evident that a similar model of HAFT applies to the covalent sulfide and selenide compounds where non-Heisenberg like superexchange or kinetic exchange interactions via different routes dominate. Competition among them may give rise to the observed non-collinear helical order [5-7].

The electronic transport in these compounds, especially those containing
Cu and Ag remains a topic of debate. Different studies have reported quite contrasting conductivity behavior, with $\rho(300K) = 0.025\Omega\text{-cm}$ in crystals [10] to immeasurably high resistivity of pure CuCrS$_2$, and with the insulator to metal transition upon V-substitution of Cr atoms etc [11]. In the previous chapters we have reported our detailed study of the electronic transport properties of CuCrS$_2$. We found non-insulating behavior contrary to previously believed insulating nature with a complex temperature dependence of resistivity $\rho$ [12, 13].

In this chapter we present the results of magnetic properties, electrical conductivity, thermoelectric power and specific heat of CuCrSe$_2$. Our results clearly show non-insulating nature of these compounds similar to CuCrS$_2$. To the best of our knowledge the magnetic properties, transport properties with the specific heat results of CuCrSe$_2$ have been reported measured for the first time.

5.2 Experimental

5.2.1 Preparation

CuCrSe$_2$ was prepared directly from the reaction of pure elements Cu(4N), Cr(4N) and Se(4N) in the required atomic ratio in a sealed quartz tube. The initial reaction, carried out at lower temperatures, by slow heating upto 650$^0$C, gave significant contamination of the ferromagnetic compound CuCr$_2$Se$_4$. After the initial reaction the mass was thoroughly ground and pelletized under pressure of 5 ton. Subsequent sintering of pellets above 900$^0$C in sealed tube over 5-7 days, followed by air quenching completely eliminated the ferromagnetic phase, as could be checked by the magnetization measurement at room temperature. Three samples were prepared: Samples 1, 2 (Se1, Se2) were prepared by sintering at 900$^0$C. Sample2
(Se2) contained less than 1% ferromagnetic impurity phase CuCr$_2$Se$_4$ as confirmed by M-H measurement at 2 K. Sample3 (Se3) was prepared at higher temperature of 1100°C, and is denoted as the H.T. phase. We also tried to grow single crystals of CuCrSe$_2$ by using iodine as a transport agent but could not get the crystal flakes. Instead, we observed the growth of CrSe$_{1+x}$ ($0 \leq x \leq 0.5$) like crystals. The compounds were characterized by X-ray diffraction on powders and by EDAX attached to the SEM for chemical analysis.

5.3 X-ray Diffraction and Rietveld Refinement

The X-ray diffraction patterns of powder samples were obtained using a Philips Diffractometer with Cu($K_\alpha$) radiation. The structural parameters (atomic positions, occupancy of particular site and lattice parameters) in space group $R3m$ were calculated by Reitveld refinement of X-ray diffraction patterns using the GSAS(EXPGUI) program [14]. The position of the different atoms in the space group $R3m$ for CuCrX$_2$ are shown in Fig.5.1 where all the atoms occupy 00z positions with the rhombohedral lattice translations ($\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$) and ($\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$).

The refined parameters with standard deviation are presented in the table(5.1). In the L.T. phase (Se1) the refined structure was found to possess nearly full occupancy of Cr(I)($z = 0$) and Cu($z \approx 0.15$) on alternate layers. In H.T. phase (Se3) significant vacancies of Cr(I) layers (with $n \approx 0.90$) with additional occupancy of ($n \approx 0.1$) interlayer Cr(II) ($z \approx 0.5$) within Cu-layers were found. These interstitial Cr(II) atoms will be shown in our later discussion to have important effects on the transport and magnetic properties of H.T. phase. It should be noted that we have used combined occupancy of Cr(I) and Cr(II) as 1 and refined the structural parameters.
These particular choices gave the least values of $R(F^2)$ and $\chi^2$ for the H.T. phase (Se3). The calculated, observed and error patterns are presented in Fig.5.2 for both the samples. The results show a decrease in the lattice parameters of the H. T. phase Se3 (sintered at $1100^\circ$C) and about 10% occupancy of total chromium in the interlayer octahedral positions Cr(II). Chemical analysis showed the atomic percentages to be within 5% of the stoichiometric amount for all the samples.

Figure 5.1: Unit cell of CuCrSe$_2$ showing layered structure. Cr(I) is the regular sites while Cr(II) sites are partially occupied in a disordered phases.
Figure 5.2: Calculated, observed and error patterns for the Se1(900°C) and Se3(1100°C) phases refined by GSAS (EXPGUI) program.

Table 5.1: Refined structural parameters of CuCrSe₂ (space group R3m) using GSAS (EXPGUI).

<table>
<thead>
<tr>
<th>Atom</th>
<th>L.T (phase)</th>
<th>H.T. (phase)</th>
<th>Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>z</td>
<td>Occupancy</td>
<td>z</td>
</tr>
<tr>
<td>Cr(I)</td>
<td>0</td>
<td>1.00</td>
<td>Cr(I)</td>
</tr>
<tr>
<td>Cr(II)</td>
<td>0.50(5)</td>
<td>0.0</td>
<td>Cr(II)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.142(2)</td>
<td>1.00</td>
<td>Cu</td>
</tr>
<tr>
<td>Se(I)</td>
<td>0.260(1)</td>
<td>1.00</td>
<td>Se(I)</td>
</tr>
<tr>
<td>Se(II)</td>
<td>0.740(1)</td>
<td>1.00</td>
<td>Se(II)</td>
</tr>
<tr>
<td>a = 3.6848(3)Å, c = 19.428(1)Å</td>
<td>a = 3.680(4)Å, c = 19.394(2)Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>χ² = 0.26, R(F²) = 0.0854</td>
<td>χ² = 1.03, R(F²) = 0.0641</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POR = 0.66</td>
<td>POR = 0.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

§1 Preferential Orientation Ratio(POR)
5.4 Electronic Transport Properties

5.4.1 Electrical Resistivity

The electrical resistivities ($\rho$ vs. $T$) of three samples of CuCrSe$_2$ are presented in Fig. 5.3. We find weak signature of the antiferromagnetic transition on $\rho$ in all the samples. In the inset we have plotted derivative of resistivity $\frac{d\rho}{dT}$ with temperature for near the magnetic transition temperature. Sharp change in $\frac{d\rho}{dT}$ are visible at $T_N$.

Figure 5.3: Resistivity $\rho$ of three samples of CuCrSe$_2$ (Se1, Se2 and Se3) plotted as ($\rho$ vs. $T$) show metallic temperature dependence for most ordered phase Se1 with weak anomaly in $\rho$ at $T_N$. Inset $\frac{d\rho}{dT}$ vs. $T$ plot of sample Se1 clearly show divergence at 55 K.

The samples (Se1, Se2) prepared at 900°C show metallic temperature dependence of resistivity down to 2 K without significant effects due to ordering at $T_N$. The divergence like (sharp change) nature of $\frac{d\rho}{dT}$ at $T_N = 55$ K.
as shown in the inset, is surprisingly similar to that found at the magnetic transition in metallic ferromagnets like Ni and Gd etc. Similar effects are also seen in the chemically related Cr-chalcogenide spinels of CuCr₂X₄(X=S, Se or Te) at their magnetic transitions \(T_C = 320 - 460\) K [17].

The larger resistivity and smaller residual resistivity ratio \(\rho_{300}/\rho_{4.2}\) (RRR) of about 3 in Se2, compared to the RRR value 5 for Se1 sample is the result of about 1% ferromagnetic impurities in Se2, while sample Se1 is free from the ferromagnetic impurities as found from \(M(H)\) measurement at room temperature. The high temperature (H.T.) sintered phase Se3 has significant disorder in the occupancy of chromium atoms. In it about 10% of the chromium atoms occupy the interlayer octahedral sites after treatment at high temperature of 1100°C (see section 5.3). The value of room temperature \(\rho\) of H.T. phase is largest among the three samples, it shows a rise on cooling to low temperatures with a minimum in \(\rho\) around 150 K.

5.4.2 Hall Measurement

The Hall coefficient \(R_H\) was measured on thin circular pellets of CuCrSe₂ (Se1 & Se2) from 2K to 300K. The Hall-mobility of the carriers, \(\mu_H\), was calculated from \(R_H/\rho\) and its dependence on temperature is plotted in the Fig.5.4. The positive sign of Hall resistivity indicates hole type conduction and is in agreement with the sign of thermoelectric power. The room temperature \(\mu_H\) is around 20\(cm^2/Vs\) and the hole carrier density is \(1.7 \times 10^{20}/cm^3\), in the range of heavily doped semiconductors. The \(\mu_H\) increases on cooling towards the ordering temperature \(T_N \approx 55K\) in Se1 and shows a sharp increase below \(T_N\). On the other hand, sample Se2 (with impurity phase CuCr₂Se₄) shows a weak temperature dependence down till 2 K. We have not done Hall measurements in the H.T. phase Se3.
Figure 5.4: Hall mobility $\mu_H$ for the CuCrSe$_2$ samples (Se1 & Se2) show sharp rise in the ordered state for pure phase Se1 and a weak temperature dependence for Se2 in which 1% impurity phase was detected.

5.4.3 Thermoelectric Power

In Fig.5.5 we have presented the Seebeck coefficient $S$ of the CuCrSe$_2$ samples. In spite of their metallic nature, $S$ is remarkably large and tends towards a constant value at high temperature as also found for CuCrS$_2$ compounds (see previous chapters). The room temperature thermopower $S$ is around $+100\mu VK^{-1}$ and corresponding electrical resistivity $\rho$ (300K)$\approx 1.8m\Omega cm$, which is significantly lower than CuCrS$_2$ compounds.
Figure 5.5: The thermoelectric power $S$ vs. $T$ of CuCrSe$_2$ (Se1, Se2 and Se3) samples. Large value and nearly saturating behavior of $S$ at high temperature is seen.

5.5 Magnetic Properties

In Fig.5.6a, we show the magnetization $M(T)$ results of CuCrSe$_2$ with CuCrS$_2$ at 1kOe magnetic field and in Fig.5.6b the isothermal magnetization $M(H)$ at 1.8 K for both the samples. In the inset of Fig.5.6a, we have shown magnetization results of the H.T. phase (Se3) of CuCrSe$_2$, in which about $\approx 10\%$ of Cr-layer atoms are transferred to the Cu containing layers after prolonged sintering at 1100°C.
In all the compounds a maximum in magnetization is observed at low temperatures (Fig.5.6a). If we compare the results of CuCrS$_2$ and CuCrSe$_2$ we find a sharp cusp like anomaly at the antiferromagnetic transition of CuCrS$_2$ while the maximum at the transition in CuCrSe$_2$ is well rounded: In both cases the magnetization in 1kOe field is reversible after cooling under field (FC) and zero field-cooling (ZFC). This, however, is not the case for the H.T. phase (Se3) of CuCrSe$_2$ as shown in the inset of Fig.5.6a. The magnetization (Se3) clearly shows a field cooling effect (splitting of FC and ZFC curves below 22 K). This irreversibility may be related to a spin-glass like transition at 22 K in this sample due to significant disorder in the occupancy of Cr atoms. This disorder also causes a large increase
in the paramagnetic susceptibility, as there is about 5-fold increase in its susceptibility compared to the Se1 sample at 55 K. We believe that the interstitial occupancy results in random clustering of Cr atoms. The increase in paramagnetic susceptibility is due to ferromagnetic correlations among the atoms of the cluster. At low temperatures the random nature of inter-cluster interactions causes spin-glass like freezing seen in the sharp drop in the magnetization below 22 K in zero field cooled (ZFC) measurement. A detailed study of the magnetic and specific heat properties of this sample has not been done. In the following we will report the properties of Se1(L.T) for which the Cr-lattice disorder is absent and $M(T)$ behaviour is reversible under ZFC & Fc.

For both S & Se compounds, the high temperature magnetic susceptibility follows a Curie-Weiss (CW) temperature dependence as marked by the dotted curve in Fig.5.6a from 100 K to 300 K. The Curie-Weiss (CW) susceptibility $\chi$ is given as

$$\chi = C/(T - \theta_{CW})$$  \hspace{1cm} (5.1)

Where C is the Curie constant and $\theta_{CW}$ is the asymptotic Curie-Weiss temperature. The value of $C$ is 1.9 and 2.9 and $\theta_{CW}$ is -110 K and +5 K respectively for sulfide and selenide compounds. The higher value of C as compared to expected value of 1.87 for Cr$^{3+}$ ions with $S = 3/2$, clearly shows that ferromagnetic correlations exist among Cr ions in the paramagnetic phase of CuCrSe$_2$ at least up to 300 K. This clearly predicts that the interactions between the bare moments of Cr ions are much stronger and a small value of $\theta_{CW} = +5$ K which was obtained in this case by the fitting of the data below 300 K and may be the result of the effective cancellations from the distant neighbors. In a previous study of AgCrSe$_2$ a values
of $C=1.6$ and asymptotic (CW) temperature $\theta_{CW} = +50$ K was deduced from the fitting of the susceptibility data between 316 K and 400 K [18].

The change in the sign of $\theta_{CW}$ from $-110$ K in CuCrS$_2$ to $+5$ K in CuCrSe$_2$ may be due to the weakening of the direct antiferromagnetic interactions with the increase in the Cr-Cr separation in selenide compounds which favors the indirect exchange, which is ferromagnetic within the layers [1, 2]. It is most interesting to note that the change in the magnetic interactions has relatively small effect on the ordering temperature; this may be related to the interlayer interactions which are different from the intralayer interactions in these layered compounds. The observed upturn in the $M(H)$ plots see in Fig.5.6b, above 5 T and 1.5 T respectively for CuCrS$_2$ and CuCrSe$_2$ is a clear indication of the non-collinear magnetic order in these systems due to competing interactions between the distant neighbors.

### 5.6 Specific Heat

The temperature dependence of specific heat $C_p(T)$ is presented in the Fig.5.7a for both the compounds CuCrS$_2$ and CuCrSe$_2$. In the case of CuCrS$_2$ the specific heat exhibits a clear peak at the magnetic transition $T_N = 38$ K. This corresponds to a structural transition from rhombohedral to monoclinic phase as was earlier observed by neutron and synchrotron diffraction [8]. A latent heat contribution in $C_p$ probably due to a similar lattice distortion was also reported for AgCrS$_2$ [9]. In both CuCrS$_2$ and AgCrS$_2$ the change in magnetic entropy below $T_N$ was about 70% of the value that is expected for 3-dimensional magnetic ordering of the Cr$^{3+}$ spins.

In the case of CuCrSe$_2$ no sharp peak is observed but a visible maximum can be seen in Fig.5.7a at $T_N = 55$ K.
Figure 5.7: (a) Specific heat $C_p(T)$ showing a lambda-like anomaly in CuCrS$_2$ and an extended maximum in CuCrSe$_2$ at the magnetic ordering temperature. (b) The large magnetic contribution to heat capacity indicating extensive short range ordering above 55 K in CuCrSe$_2$.

This feature coincides with the divergence in the derivative of resistivity.
(\(dp/dT\)) (see in the inset of Fig.5.3) and the maximum in the susceptibility \(\chi\) (see Fig.5.6a). In the Fig.5.7b, we have plotted the contribution of magnetic heat capacity for CuCrS\(_2\) and CuCrSe\(_2\).

In order to estimate the magnetic specific heat \((C_{mag})\), we subtracted the lattice contribution \((C_{ph})\) from the total heat capacity \((C_P)\) for both the cases. The lattice (phononic) contribution was calculated in the Debye model by considering Debye temperature \(\theta_D = 280\) K and 340 K respectively for CuCrSe\(_2\) and CuCrS\(_2\). At low temperature \((T \leq 10\) K\) the lattice contribution of specific heat is given by:

\[
C_{ph} \approx Nk_B(T/\theta_D)^3
\]  

(5.2)

Where \(N\) is the total number of atoms and \(k_B\) is the Boltzmann constant.

The arrows in the Fig.5.7a and Fig.5.7b mark the magnetic transition temperatures \(T_N\) of the respective compounds which correspond to the susceptibility cusp in CuCrS\(_2\) and the rounded maximum in the susceptibility in case of CuCrSe\(_2\) (Fig.5.6a). The magnetic contribution in \(C_P\) for CuCrSe\(_2\) extends much higher temperature above \(T_N\), indicating extensive short range ordering in the paramagnetic phase.

### 5.6.1 Magnetic Entropy

The magnetic entropy \(S_{mag}\) is calculated by integrating \(C_{mag}/T\) vs. \(T\) curves, and is illustrated in the Fig.5.8a for both compounds. We have drawn two separate \(S_{mag}(T)\) plots for CuCrSe\(_2\) by using two different values of Debye temperature \(\theta_D = 280\) K and 290 K in order to estimate \(C_{mag}\).

In case of CuCrS\(_2\) the magnetic entropy \(S_{mag}\) is small at low temperatures and increases rapidly near the transition due to the destruction of long range magnetic order at 38 K. \(S_{mag}\) attains about 9J/moleK at 38 K which
Specific Heat

is around 75% of the entropy for the localized moments of Cr\(^{3+}\) ions with 
\[ S = 3/2 \] [i.e. \( S_{mag} = R \ln(2S + 1) = 11.53 J/mole - K \)]. However, neutron diffraction study gave a reduced moment of 2.37\(\mu_B\)/Cr atom and a helical magnetic order. The sharp jump-like change in \( S_{mag} \) at the transition temperature (Fig.5.8a) can be related to the structural distortion which was also confirmed by another neutron diffraction study [8].

The magnetic entropy of the selenide compound CuCrSe\(_2\) shows qualitatively different behavior. \( S_{mag} \) is quite large in this case and increases rather slowly on heating from 2 K and continuously across the magnetic transition 55 K till about 80 K. The temperature dependence of \( S_{mag}(T) \) strongly suggests the absence of long range magnetic order in this compound. In the Fig.5.8b we have presented the plot of \( C_{mag} \) vs. \( T \) on a logarithmic scale along both the axis; The plot for CuCrSe\(_2\) is linear with a slope of 2, and implies that \( C_{mag} = AT^2 \) below the temperature \( T = 14 \) K, with the coefficient \( A = 9 \times 10^{-3} J/(moleK^3) \).

5.6.2 \( T^2 \)-dependence

As seen in Fig.5.8b the magnetic specific heat \( C_{mag} \) follows a \( T^2 \)-dependence upto a fairly high temperature of 14 K in CuCrSe\(_2\). A similar \( T^2 \)-dependence with nearly the same coefficient as in CuCrSe\(_2\) was reported for the V-doped sample CuCr\(_{1-x}\)V\(_x\)S\(_2\) (\( x = 0.30 \)) [11]. In the latter case, V-substitution of Cr causes bond frustration of antiferromagnetic interactions and results in a spin-glass (SG) like behaviour at a reduced temperature; this is shown by a characteristic irreversibility in the magnetization on cooling under field [11]. However, in our selenide compound a similar irreversibility due to spin glass like behavior is absent. Nevertheless, a \( T^2 \)-dependence in either case is not natural to a canonical SG phase, where instead a \( T \)-dependence below the freezing temperature is universally observed [19].
Figure 5.8: (a) Magnetic entropy of CuCrSe$_2$ showing a large value and a continuous increase across 55 K. (b) The linear curve of the logarithmic plots of $C_{mag}$ vs. $T$ for CuCrSe$_2$ at low temperature with slope 2, giving a $T^2$-dependence of $C_{mag}$ below 14 K.

A lot of work has been done on the elementary excitations of a diluted
2D antiferromagnet (e.g. Kagome spin glass SrCr$_{9p}$Ga$_{12-9p}$O$_{19}$) wherein the long-range order is inhibited by frustration (geometrical or otherwise) and at low temperature the collective excitations of the spin-liquid give $C(T) = AT^2$. This behavior was found to be surprisingly robust against the atomic substitution for increasing the bond disorder [20]. The observation of $T^2$-dependence in both the compounds CuCrSe$_2$ and CuCr$_{0.7}$V$_{0.3}$S$_2$ clearly suggests that spin-liquid like excitations also exist in case of covalent solids with non-Heisenberg magnetic interactions.

5.7 Conclusions

The electronic transport and magnetic properties of the layered antiferromagnet CuCrSe$_2$ have been presented for the first time. The electrical resistivity $\rho$ of CuCrSe$_2$ shows metallic temperature dependence from 300 K down till 2 K. The thermoelectric power is large and show saturating behavior at high temperatures similar to the sulfide compound CuCrS$_2$. The most remarkable features are in its magnetic and specific heat properties. The magnetic ordering in the selenide is quite different from the corresponding sulfide compound. The sulfide is known to undergo 3D long range non-collinear magnetic ordering with an accompanying lattice distortion below $T_N$ (38 K). On the other hand the $M(T)$ and $C(T)$ measurements on the ordered and pure phase of CuCrSe$_2$ suggest a complex short range ordering that extends till much higher temperature than $T_N = 55$ K. For the low temperature phase the absence of the irreversibility in $M$ under field cooling clearly discounts spin-glass freezing. Interestingly, here $C_{mag}$ varies as $T^2$ at low temperatures, and surprisingly similar dependence is also found in CuCr$_{1-x}$V$_x$S$_2$ for $x = 0.30$. In the latter long range non-collinear order is suppressed by lattice defects and instead a linear $T$-dependence is expected.
below the observed spin-glass freezing [11]. A $T^2$-dependence has been discussed in the context of the elementary excitations of the spin-liquid in a diluted antiferromagnet, such as 2D-Kagome spin glass SrCr$_9$P$_n$Ga$_{12-9n}$O$_{19}$) [20]. In the light of similar behavior of our largely covalent compounds in which the competing long range indirect exchange interactions can also suppress the magnetic order, a deeper understanding of the elementary excitations of the spin-glass (or a spin liquid) state is required.