Low-temperature structural and transport anomalies in Cu₂Se

Hang Chi,¹ Hyoungchul Kim,²,⁷ John C. Thomas,³ Guangsha Shi,⁵ Kai Sun,³ Milinda Abeykoon,⁴ Emil S. Bozin,⁴ Xiaoya Shi,⁴ Qiang Li,⁴ Xun Shi,⁵ Emmanouil Koupakis,⁵ Anton Van der Ven,¹,⁶ Massoud Kaviany,² and Ctirad Uher¹,*

¹Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA
²Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA
³Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA
⁴Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
⁵State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China
⁶Materials Department, University of California, Santa Barbara, California 93106, USA
⁷High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

(Received 14 March 2014; revised manuscript received 7 May 2014; published 28 May 2014)

Through systematic examination of symmetrically nonequivalent configurations, first-principles calculations have identified a new ground state of Cu₂Se, which is constructed by repeating sextuple layers of Se-Cu-Cu-Cu-Se. The layered nature is in accord with electron and x-ray diffraction studies at and below room temperature and also is consistent with transport properties. Magnetoresistance measurements at liquid helium temperatures exhibit cusp-shaped field dependence at low fields and evolve into quasilinear field dependence at intermediate and high fields. These results reveal the existence of weak antilocalization effect, which has been analyzed using a modified Hikami, Larkin, and Nagaoka model, including a quantum interference term and a classical quadratic term. Fitting parameters suggest a quantum coherence length $L$ of 175 nm at 1.8 K. With increasing temperature, the classical parabolic behavior becomes more dominant, and $L$ decreases as a power law of $T^{-0.83}$.

DOI: 10.1103/PhysRevB.89.195209

PACS number(s): 71.55.Ht, 72.15.Rn, 72.80.Jc

Transition metal chalcogenides (TMCs) allow fruitful research in contemporary condensed matter physics, leading to intriguing discoveries and promising applications [1]. For example, the silver chalcogenides (e.g., Ag₂Te) are renowned for their extraordinary large magnetoresistance (MR) [2] and have been recently identified as a new class of binary topological insulators (TI) with a highly anisotropic Dirac cone [3]. Additionally, transition metal dichalcogenides (TMDCs) $MX_2$, where $M$ is a transition metal element and $X$ is a chalcogen atom (S, Se, or Te), are well known for their two-dimensional (2D) structures formed by $X-M-X$ layers with strong in-plane bonding and weak out-of-plane interactions. The unique intrinsic 2D nature of TMDCs has stimulated the search for novel states of matter, for instance, by offering a coexistence of superconductivity and the Mott commensurate charge density wave (CCDW) phase in 1T-TaS₂ [4]. Furthermore, the electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electronic band structures of TMDCs are believed to host exotic spin-orbit phenomena such as the systematic crossover from electron density wave (CCDW) phase in 1T-TaS₂. The ground state of Cu₂Se was obtained via structural relaxation of the cubic HT $\beta$ phase of Cu₂Se [space group $Fm\bar{3}m(D_{2d}^3, #225)$] is constructed by statistically distributing Cu atoms over the 8$c$ tetrahedral sites in a face-centered cubic (fcc) matrix formed by Se atoms. However, the structural determination of the ordered phase(s) still remains controversial [11]. Furthermore, despite some rare reports on samples with quite high Cu deficiency (e.g., Cu₂₋ₓSe, 0.20 < x < 0.25) [12], a detailed study of the transport properties of stoichiometric Cu₂Se at low temperatures is still desirable. In this paper, we report first-principles determination of the ground state along with several unexpected experimental findings regarding the low-temperature transport properties of Cu₂Se, which may indicate an intrinsic 2D quantum behavior.

The ground state of Cu₂Se was obtained via structural relaxation of the cubic HT $\beta$ phase. In order to determine the most stable structure, Cu atoms were randomly distributed onto the 32$f$ trigonal sites in the fcc Se matrix, which form tetrahedrons around the 8$c$ tetrahedral sites. Note that for stoichiometric Cu₂Se, only one-quarter of the 32$f$ sites are occupied by Cu atoms. Symmetrically distinct configurations with up to eight Cu atoms have been studied based on the Cu occupancy on the sublattice [13]. Subsequent density functional theory (DFT) calculations of the formation energy have allowed us to identify stable configurations of Cu₂Se. The DFT-based energies were obtained using the Vienna Ab initio Simulation Package (VASP) [14] within the Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) for exchange and correlation [15] and using the projector-augmented wave (PAW) method [16,17]. The electronic band structure and density of states ($D_{\text{v}}$) were calculated using more advanced Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [18,19]. VASP and PHONON [20] codes were then used for the ab initio phonon calculations.

*Corresponding author: cuher@umich.edu
The total energy and Hellmann-Feynman (HF) forces were found starting from the fully relaxed configuration, such that initial ionic forces were less than $10^{-5}$ eV/Å. The ionic displacements of 0.03 Å of selected atoms were sampled along the $x$, $y$, and $z$ directions. All phonon and thermodynamic properties were predicted using a fit of interatomic force constant tensors to the calculated HF forces. Diagonalization of the dynamical matrix yields the phonon dispersion from which the density of states of states ($D_p$) was obtained. Physical properties of Cu$_2$Se are summarized in Table I, with the literature results also listed [21,22].

The proposed ground state of Cu$_2$Se crystallizes in space group $P2_1/c$ (C$_{2h}$ #14), with optimized lattice parameters $a = 7.453$ Å, $b = 4.322$ Å, $c = 6.880$ Å, $\alpha = 90.00^\circ$, $\beta = 70.62^\circ$, $\gamma = 90.00^\circ$, and atomic occupation Cu1 (0.06111, 0.58259, 0.15164), Cu2 (0.80599, 0.92292, 0.05310), and Se (0.28070, 0.93855, 0.25485). As shown in Fig. 1(a), the ground state of Cu$_2$Se has quasi-2D characteristics typified by the Se-Cu-Cu-Cu-Se type of sextuple layers (thickness $t = 3.95$ Å), which are interconnected via weak Se-Se bonds (gap $\delta = 3.08$ Å). Compared with recent literature results using rather different approaches, the monoclinic structure of Cu$_2$Se obtained here has lower formation energy per unit formula (Table I) [10,23]. The proposed structure is also dynamically stable due to the absence of the soft modes in the phonon spectrum, as is evident in Fig. 1(d). As shown in Fig. 1(e), the monoclinic Cu$_2$Se is confirmed to be semiconducting, and the electronic band gap $E_g$ (using HSE) is found to be 1.03 eV, which agrees very well with the experimental value of 1.20 eV [21] and is the best first-principles result in comparison to the existing literature values [24].

Polycrystalline Cu$_2$Se samples were prepared following the recipes described elsewhere [10]. Powdered samples were used for the temperature-dependent x-ray diffraction (XRD) experiments at the X17A beamline of the National Synchrotron Light Source at the Brookhaven National Laboratory. The setup utilized cylindrical geometry with an x-ray beam of 67.42 keV ($\lambda = 0.1839$ Å), a Perkin-Elmer image plate detector placed perpendicular to the primary beam path $d = 204.134$ mm away from the Kapton capillary containing the pulverized sample, and an Oxford Cryosystem 700 for temperature control. A JEOL 2010F transmission electron microscope (TEM) operating at 200 kV was used to collect selected area electron diffraction (SAED) patterns for the analysis of the detailed microstructure. Simulated SAED patterns were obtained using the CrystalKit software package.

<table>
<thead>
<tr>
<th>$\Delta E_0$</th>
<th>$E_g$</th>
<th>$u_{p,e,A}$</th>
<th>$c_p$</th>
<th>$c_{11}$</th>
<th>$c_{22}$</th>
<th>$c_{33}$</th>
<th>$c_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$Se</td>
<td>0</td>
<td>1.03</td>
<td>2635</td>
<td>72.1</td>
<td>11.14</td>
<td>102.49</td>
<td>88.62</td>
</tr>
<tr>
<td>Literature</td>
<td>0.003</td>
<td>0.046</td>
<td>1.20</td>
<td>2918</td>
<td>81.6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cu$_2$Se</td>
<td>14.65</td>
<td>12.82</td>
<td>6.81</td>
<td>6.90</td>
<td>42.37</td>
<td>3.95</td>
<td>3.95</td>
</tr>
<tr>
<td>Literature</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$P$_{21}/c$ structure, from Ref. [23].
$^b$C$_2$/c structure, from Ref. [10].
$^c$From Ref. [21].
$^d$From Ref. [7].
$^e$From Ref. [22].
starts to affect the structure \[25\]. vacancy ordering at finite temperature when thermal energy the different packing order of the sextuple layers and/or Cu-
Additional superstructural diffraction spots/stripes have been verified the predicted layered structure of the ground state. SAED pattern along the monoclinic \[12,25–28\], a reversible measurement between the experimental and theoretical patterns has

To further understand the structure, low-temperature XRD measurements have been performed. In line with earlier reports \[12,25–28\], a reversible \(\alpha\) to \(\alpha'\) superstructure transition is also evident in the sample studied here via an intensity rearrangement of the multiplet of superlattice peaks located in the \(Q\) region close to the (400) reflection in cubic notation (Fig. 2). This is found from the assessment of the systematic temperature-dependent XRD data, collected in the 100–300 K range upon warming. The transfer of intensity occurs at around 175 K (upper right inset in Fig. 2).

We were interested to find out what the impact is of such structural changes on the transport properties. As shown in Fig. 3, the above mentioned \(\alpha\) to \(\alpha'\) type of transition has a strong imprint on the temperature dependence of the electrical resistivity (20% effect) and the Hall effect. The electrical resistivity of Cu\(_2\)Se exhibits a highly anomalous behavior in the 100–150 K temperature range, which is also accompanied by a large peak in the Hall effect. We speculate that such features might represent a possible charge density wave (CDW) transition [29] as a result of the distortion/redistribution of the sextuple layers upon temperature change. However, further theoretical and experimental efforts are needed to clarify the issue. We note that in spite of looking for accompanying anomalies in the Seebeck effect, thermal conductivity, and the specific heat, we found none. The anomalous behavior seems to be limited to galvanomagnetic transport only.

At even lower temperatures (1.8–30 K), the MR of Cu\(_2\)Se is extraordinary, as shown in Fig. 4(a). The semiclassical transport theory predicts a quadratic field-dependent MR in the low-field range, which saturates in high fields. In distinct contrast to the traditional theory, the MR of Cu\(_2\)Se at low temperatures exhibits a WAL-like cusp, which is suppressed when the temperature increases. In addition, at high fields, the MR increases with the increasing field in a linear fashion with no sign of saturation up to \(B = 5\) T.

We account for the field dependence of differential magnetoconductance (MC) over the entire range of fields and...
where $\psi$ is the digamma function. The original formalism of the simple HLN model was developed to characterize the transport properties of a 2D system where the conductance quantum $(2e^2/h)$ naturally comes into play. In order to compensate for the bulk effects of this quasi-2D layered structure of Cu$_2$Se, we have normalized the conductance using the zero field value and introduced a dimensionless fitting parameter $\alpha$. Here $L$ is the phase coherence length, and $\beta$ is the quadratic coefficient arising from additional scattering terms. The HLN model has been successfully used in explaining the magnetotransport phenomena in various 2D material systems like Bi$_2$Se$_3$ [32,33], Bi$_2$Se$_2$Te [34], and Bi$_2$Te$_2$Se thin films [31]. It is worth emphasizing that such a modified model simultaneously accounts for the quantum phase interference cusp at low fields as well as the linearlike MR at high fields. It is shown that the additional quadratic term compensates the logarithmic dependence of the quantum interference at high fields, leading to an intermediate linear field dependence of MR. The overall fitting result, along with the corresponding quantum interference term and quadratic term, is shown in Figs. 4(b) and 4(c) for $T = 1.8$ K and 9 K, respectively. In the present sample, the phase coherence length $L$ is 175 nm at 1.8 K and decreases following a power law of $T^{-0.83}$ temperature dependence. The successful application of the HLN model in Cu$_2$Se is advocating for the 2D quantum nature of the new phase and likely provides another candidate of bulk materials with monolayer behavior, apart from the newly discovered ReS$_2$ [35].

In summary, the ground state of Cu$_2$Se, typified by Se-Cu-Cu-Cu-Cu-Se sextuple layers, has been identified using ab initio calculations. Upon cooldown to liquid nitrogen temperatures, the transport property measurements along with the structural analyses have confirmed the existence of yet another phase transition of possible CDW character. The unusual manifestation of the WAL-type of MR profile at liquid helium temperatures indicates the quantum nature of such a phase of Cu$_2$Se, which may promote further interest in this member of the TMCs.

This work was supported as part of the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC-0000957. The JEOL 2010F TEM was funded by the National Science Foundation (Grant No. DMR-9871177) and operated by the Electron Microbeam Analysis Laboratory at the University of Michigan. Work at Brookhaven National Laboratory was supported by the DOE, Office of Science, Division of Materials Science (Contract No. DE-AC02-98CH10886). Work at the Shanghai Institute of Ceramics was supported by the National Natural Science Foundation of China (NSFC) (Award No. 51121064 and 51222209).

FIG. 4. (Color online) (a) Magnetoresistance profile (as a function of magnetic field intensity) of Cu$_2$Se at various temperatures (1.8–30 K) indicating evolution of weak antilocalization behavior as the temperature is lowered to 1.8 K. Theoretical fitting to differential magnetoconductance using a modified HLN model at selected temperatures (b) 1.8 K and (c) 9 K. The inset of (c) depicts the fitting parameters showing a power law behavior ($\sim T^{-0.83}$) of the quantum interference length.

temperatures with a modified Hikami, Larkin, and Nagaoka (HLN) quantum interference model [30,31]:

$$ MC \equiv \frac{G(B) - G(0)}{G(0)} = -\alpha \left[ \psi \left( \frac{\hbar}{4eL^2B} \right) + \frac{1}{2} \ln \left( \frac{\hbar}{4eL^2B} \right) \right] + \beta B^2, $$


