Exotic Magnetic and Electronic Properties of Layered CrI$_3$ Single Crystals Under High Pressure

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Through advanced experimental techniques on CrI$_3$ single crystals, we derive a previously not discussed pressure-temperature phase diagram. We find that $T_c$ increases to ~ 66 K with pressure up to ~ 3 GPa followed by a decrease to ~ 10 K at 21.2 GPa. The experimental results are reproduced by theoretical calculations based on density functional theory where electron-electron interactions are treated by a static on-site Hubbard $U$ on Cr 3$d$ orbitals. The origin of the pressure induced reduction of the ordering temperature is associated with a decrease of the calculated bond angle, from 95° at ambient pressure to ~ 85° at 25 GPa. Above 22 GPa, the magnetically ordered state is essentially quenched, possibly driving the system to a Kitaev spin-liquid state at low temperature, thereby opening up the possibility of further exploration of long-range quantum entanglement between spins. The pressure-induced semiconductor-to-metal phase transition was revealed by high-pressure resistivity that is accompanied by a transition from a robust ferromagnetic state to gradually more dominating anti-ferromagnetic interactions and was consistent with theoretical modeling.

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Two-dimensional (2D) van der Waals (vdW) materials offer a plethora of functional properties that are not only of fundamental interest but are essential for the development of new technological applications[1–3]. Layered chromium trihalides emerged as potential 2D vdW materials with unique layer-dependent magnetic properties[4, 5]. Understanding the long-range magnetic order in these 2D materials is an intriguing subject of widespread research. According to the Mermin-Wagner theorem[6], it is strongly suppressed in a 2D isotropic Heisenberg system due to spin fluctuations at any finite temperature. Here, the magnetocrystalline anisotropy (MCA) comes to the rescue and stabilizes the long-range magnetic order in CrI$_3$_[7–11]. Several experiments and theories have been put forward, reflecting the role of I-5$p$ state spin-orbit coupling (SOC) strength in the origin of the MCA through the Cr 3$d$-I 5$p$-Cr 3$d$ superexchange interaction. This interaction is mediated by I-ions octahedrally coordinating with Cr ions with an in-plane Cr-I-Cr bond angle of 95°. According to the Goodenough-Kanamori-Anderson (GKA) rule, the magnetic interaction is primarily ferromagnetic (FM) when the metal-ligand-metal bond angle is 90°[12]. Therefore, the Cr-I-Cr bond angle plays a significant role in understanding the long-range FM superexchange interaction[13], as well as the MCA. Further modification in the bond angle should have a substantial impact on the electronic, magnetic, and transport properties of CrI$_3$. Theoretical calculations of a favorable magnetic ground state in monolayer CrI$_3$ are not too conclusive, as they suggest both FM[14] and anti-ferromagnetic (AFM)[15] ground states under lattice compression. However, a more recent calculation suggests that depending on the anisotropy of the in-plane lattice strains, both these ground states can co-exist with a possibility of a complete quenching of the magnetic order at a critical isotropic lattice compression[16]. Experimentally, an increase in the FM $T_c$ with pressure was attributed to a possible decrease in the Cr-I-Cr bond angle towards 90°[17]. However, with a maximum pressure of only 1 GPa, the variation of $T_c$ in a broader range of pressures eluded experimental detection. This prohibits an experimental analysis of the possible decrease in the Cr-I-Cr bond angle below 90°, and its influence on the strength of the Cr-Cr superexchange interaction and $T_c$.

The experiments reported here go up to ~ 40 GPa, and...
FIG. 1: (a) Temperature-dependent Raman spectra measured with circularly polarized light in parallel polarization configuration (see SI for detailed analysis) (b) Pressure-dependent Raman spectra at 300 K measured at parallel polarization configuration. (c) Raman shift of all the phonon modes with pressure obtained from the spectra presented in panel (b). Red dashed line shows the pressure above which blue shift and smearing of peaks occur. Calculated structure (d) at 0 GPa and (e) at 25 GPa.

offer completely new possibilities to tune the $T_c$, phonon dispersions, electronic, magnetic, and magneto-transport properties of CrI$_3$ single crystals. Overall, understanding the correlation between the bond-angle and various magnetic and electronic properties is questionable and elusive. Here, we provide a comprehensive answer to this question for CrI$_3$ through combined complementary experimental and theoretical studies[18]. We observe, a hitherto unexplored, pressure-induced semiconductor-to-metal (SM) phase transition and possibly a Kitaev spin-liquid (KSL) phases in CrI$_3$ single crystal samples.

Temperature-dependent Raman spectra at ambient pressure shows a FM to paramagnetic ($T_c$) and rhombohedral ($R3$) to monoclinic ($C2/m$) structural ($T_s$) transitions at $\sim 60$ K and $\sim 210$ K[19], respectively (see Fig.1(a) and for detailed analysis of Raman experiment see SI[18]). The obtained ambient pressure Raman spectra are in excellent agreement with theoretically obtained spectra of perfect crystals, suggesting a high crystalline purity of the synthesized material[20–22]. Pressure-dependent Raman spectra reported here, see Fig.1(b), presents only small variation in the optical phonon frequencies up to 4.4 GPa. While above 4.4 GPa in Fig.1(c), a sizable blue shift with a significant decrease in intensities of all the optical phonon frequencies is observed. Additionally, above this pressure, the distinctive phonon spectral features begin to smear out into broad features, and the $A_2^g$ and $A_6^g$ phonon modes are gradually suppressed and disappear above 7.2 GPa. Above 17.1 GPa, the rest of all the phonon modes are suppressed, which is indicative of a pressure induced deformation / distortion of the lattice. The phonon modes, re-appear when the pressure is released to near-ambient conditions. However, a broad feature near 175 cm$^{-1}$ appears when pressure is released to 0.1 GPa, which is reminiscent of a high-pressure phase and suggest that the
FIG. 2: (a) Real and imaginary (inset) part of ac susceptibility as a function of frequency of the oscillating field, $H_{AC} = 2$ Oe. (b) Pressure dependent real part of the ac susceptibility plots at a magnetic field of $H_{AC} = 3.86$ Oe oscillating at a frequency of $f = 10$ Hz of crystal (S2). (c) $d\chi'/dT$ plot of the data shown in (b), stacked over one another for clarity. Solid black lines represent Gaussian fit to find the minimum which represent $T_c$ and in agreement with the arrows in (b) and plotted in (d). The error bars represent the computational error in the Gaussian fit. Data points from[17] are shown for comparison.

To understand the magneto-transport properties and the fate of magnetic ordering at high pressures beyond the numerous studies in magnetoresistance (MR)[25, 26], we have carried out MR measurements at different high pressures. Figure 3(a-c) illustrates the field-dependent MR at various temperatures and 21.2, 24.0, and 37.8 GPa, respectively. A negative MR can be explained as a consequence of suppressed spin-spin scattering in a FM ordered state[27]. Since the current is applied along the sample plane, the incoming electrons’ spin will always experience a lattice with parallel spin configuration (due to intra-layer ferromagnetism) below $T_c$. MR can increase (positive MR) if the in-plane spins in the lattice are disordered (i.e. not primarily FM). At 21.2 GPa, the negative MR fairly saturates at high magnetic fields and temperature below 20 K, with the minimum at 10 K, indicating that the onset of the FM ordered state should lie near 10 K. At 24 GPa in Fig. 3(b), no saturation in the negative MR is observed even up to the lowest measured temperature. However, an initial negative downturn of low-temperature curves suggests that there could be a few FM-ordered spins. Interestingly at 37.8 GPa in Fig. 3(c), we do not observe any negative MR, therefore indicating a substantial quenching of FM ordering down to the minimum measured temperature, 2 K. A positive, non-saturating MR, even at 9 T magnetic field, stems from the enhanced spin-spin scattering possibly due to the disordered spins. Since the FM $T_c$ also decreases with increase in pressure above 3 GPa, the disordered spin state is not limited to the surface, rather it’s a bulk property. Our present results show the emergence of such a magnetically quenched state in the region above 22 GPa. This pressure is equivalent to an isotropic compressive lattice strain of 14% as compared to that of 5% in monolayer CrI$_3$[16]. Such a magnetically quenched state in an in-plane honeycomb lattice, like CrI$_3$, is intriguing in the context of the topological KSL phase[28–30].
FIG. 3: Field-dependent MR under 21.2 GPa (a), 24 GPa (b), and 37.8 GPa (c). (d) Temperature-dependent resistivity at high pressure, illustrating a semiconductor to metal transition above 21.2 GPa.

Fig. 3(d), our data shows a change in the slope of the resistivity curves above 21.2 GPa, which resembles a transition to a metallic state above 21.2 GPa (with the hole as the majority charge carrier shown in Fig. S8) [18], in agreement with the pressure-induced broadening of Raman peaks in Fig. 1(b) that we interpret are due to metalization. These measurements reveal that the quenching of magnetic ordering concurrently evolves in the metallic state.

Our spin-polarized DFT also corroborate with the SM transition. In Fig. 4(a), the conduction band minimum is constituted of spin-polarized up-spin channels of Cr-3d and I-5p states. It can be seen that the band-gap is mainly originated between the I-5p state in the valence band and the Cr-3d state in the conduction band, resulting in a band-gap 0.96 and 2.68 eV for the spin-up and spin-down electrons, respectively (see Figs. S9 and S10). The projected density of states (PDOS) under 25 GPa, Fig. 4(b), show a symmetric, unpolarized spin-up and down channels, which also corroborates with the evolution of positive MR above 24 GPa due to enhanced spin-spin scattering from the non-FM spin orientation of the sample. Our calculations suggest a decrease in the Cr-I-Cr bond angle and Cr-I bond length with pressure. As a consequence, the magnetic ordering is highly suppressed in concurrence with a transition to a metallic phase at high pressure. All these new, hitherto unexplored, high-pressure phases are summarized in the pressure-temperature phase diagram, Fig. 4(c). At ambient temperature, the resistivity decreases with pressure, resembling a pressure-induced transition to a metallic state. As pointed out in Fig. 3(d), we mark the metallic region above 22 GPa. The decrease in resistivity and $T_c$ with pressure occur concurrently, meaning that the magnetic ordering (primarily FM) exists in the semiconducting phase, below 21 GPa. Furthermore, in the metallic regime (above 22 GPa), the quenching of FM ordering at low temperature reflects a possible KSL state (shaded region in Fig. 4(c)), as also pointed out in various calculations in [16, 30, 31].

Summary and outlook. We have mapped out a pressure-temperature phase diagram of CrI$_3$ up to 40 GPa. We observe, from combined advanced experimental and theoretical investigations, a pressure-induced SM transition, that is accompanied by a transition from a robust ferromagnetic state to gradually more dominating anti-ferromagnetic interactions. This makes CrI$_3$ a rather unique material, since normally such electronic transitions show exactly the opposite trend (anti-ferromagnetic interactions turning ferromagnetic). From spin-polarized DFT, we reveal a decrease in the Cr-I-Cr bond angle from 95$^\circ$ at ambient pressure to 85$^\circ$ at 25 GPa. The pressure-induced variation in the bond angle affects the FM superexchange interaction and leads to the non-monotonic variation in the $T_c$ with pressure. The quenching of ferromagnetic ordering temperature, observed here, represents a possible Kitaev spin-liquid state at low temperature and high pressure, in agreement with recent theories. Our electronic structure calcula-
tions support the experimental observation and show the emergence of a finite DOS, primarily contributed by the Cr 3d states, at the Fermi level at and above 25 GPa. The realization of the KSL state offers tremendous promise for quantum computing and quantum information through the principle of long-range spin-entanglement without the formation of static long-range magnetic ordering in magnetically frustrated systems. The present study will therefore open up new possibilities of extensive research to explore the low-temperature, high-pressure metallic phase, and further calculations of CrI₃ and similar 2D materials.

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