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Massless Dirac magnons in the two dimensional van der Waals honeycomb magnet CrCl₃

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Abstract

Two dimensional van der Waals ferromagnets with honeycomb structures are expected to host the bosonic version of Dirac particles in their magnon excitation spectra. Using inelastic neutron scattering, we study spin wave excitations in polycrystalline CrCl₃, which exhibits ferromagnetic honeycomb layers with antiferromagnetic stackings along the *c*-axis. For comparison, polycrystal samples of CrI₃ with different grain sizes are also studied. We find that the powder-averaged spin wave spectrum of CrCl₃ at *T* = 2 K can be adequately explained by the two dimensional spin Hamiltonian including in-plane Heisenberg exchanges only. The observed excitation does not exhibit noticeable broadening in energy, which is in remarkable contrast to the substantial broadening observed in CrI₃. Based on these results, we conclude that the ferromagnetic phase of CrCl₃ hosts massless Dirac magnons and is thus not topological.

1. Introduction

Ferromagnets with two-dimensional (2D) van der Waals honeycomb structures are attracting a great deal of research interests in condensed matter physics thanks to their potential for dissipationless spintronic applications [1–8]. In these materials, chemically stable atomic layers are stacked on top of each other via weak van der Waals forces allowing relatively easy exfoliation of single monolayers. The intrinsic 2D ferromagnetism was first observed in Cr₂Ge₂Te₆ and CrI₃ where the Curie temperatures remain finite down to their monolayer limits [2, 3]. These experimental results demonstrate that the magnetic anisotropy in these 2D materials are strong enough to overcome thermal fluctuations inherent in low-dimensional magnets [9, 10]. In CrI₃, the interlayer exchange couplings between ferromagnetic layers were observed to change from ferromagnetic to antiferromagnetic as the number of stacked monolayers decreased [11–14]. Such remarkable behavior

is ascribed to the changes in the mode of stacking, for instance, from rhombohedral to monoclinic. Similar stacking-dependent 2D orderings were soon observed also in isostructural CrBr₃ and CrCl₃ [4, 15, 16].

While the above discoveries raise hopes for 2D spin devices for spintronics [17, 18], to realize such practical applications it is important to understand their thermal properties in detail. Thermal excitations in long-range ferromagnetic ordered materials appear as spin waves, or magnons as their quantized units. Given the structural similarity, the magnon band structures of honeycomb ferromagnets are expected to look analogous to the electronic band structure of graphene [19, 20]. The latter is well known to exhibit linear energy-momentum relations ($E \propto p$) near its Fermi energy, where conduction electrons behave as relativistic massless Dirac particles overcoming wave-particle duality [21]. It was thus predicted that the bosonic version of Dirac particles, or Dirac magnons, should also appear on the magnon bands of honeycomb ferromagnets [20]. Such linear

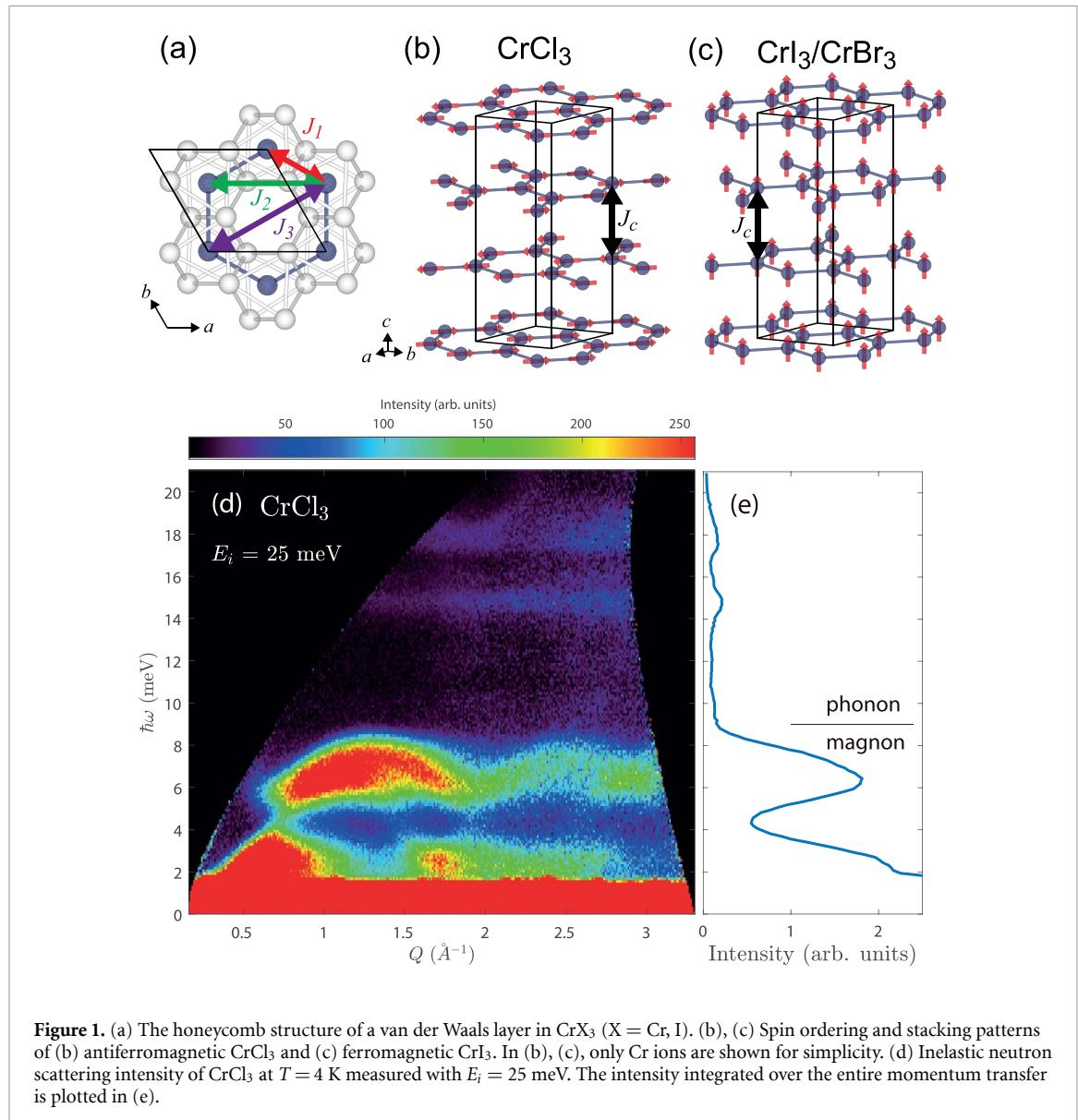


Figure 1. (a) The honeycomb structure of a van der Waals layer in CrX_3 ($X = \text{Cr}, \text{I}$). (b), (c) Spin ordering and stacking patterns of (b) antiferromagnetic CrCl_3 and (c) ferromagnetic CrI_3 . In (b), (c), only Cr ions are shown for simplicity. (d) Inelastic neutron scattering intensity of CrCl_3 at $T = 4$ K measured with $E_i = 25$ meV. The intensity integrated over the entire momentum transfer is plotted in (e).

magnon dispersion relations have experimentally been observed earlier in CrBr_3 [22], and more recently in CoTiO_3 [23, 24] and a three dimensional antiferromagnet Cu_3TeO_6 [25, 26]. In the spintronic transport, one of the key research interests lies in whether or not these Dirac magnons will be massive and thereby open an insulating gap in the bulk bands. If the bulk gap opens by breaking the time-reversal symmetry at the Dirac point, the accompanying edge states will be gapless allowing topological transport [27, 28]. One of the best examples of such topological band structure is found in 2D graphene, where spin-orbit coupling opens a small electronic band gap (~ 1 μeV) at its six-fold Dirac wave vectors, $Q = (\frac{1}{3}, \frac{1}{3})$. In the case of honeycomb ferromagnets, the antisymmetric Dzyaloshinskii-Moriya (DM) interactions between the next nearest neighbor spins may open topological energy gaps at the magnon Dirac points [29]. The resultant magnon band structure will be separated into two, one higher and the

other lower in energy, in which Berry curvatures are integrated to the integer Chern numbers $C^\pm = \pm 1$, respectively [30]. Recently, finite energy gaps were indeed observed in the magnon bands of CrI_3 [5, 6, 31] and CrBr_3 [32], respectively, indicating that the Dirac magnons in these ferromagnets are massive and topological.

CrCl_3 is unique among these van der Waals honeycomb ferromagnets because in the magnetically ordered phase its spins lie within the honeycomb planes and the adjacent monolayers are antiferromagnetically coupled (see figures 1(a) and (b)) [33, 34]. These properties are in contrast to CrI_3 , CrBr_3 and $\text{Cr}_2\text{Ge}_2\text{Te}_6$ where spins are oriented perpendicular to the honeycomb planes and coupled ferromagnetically between monolayers (see figure 1(c)). Since its spins are lying in the plane, CrCl_3 is expected to host massless Dirac magnons without gap openings at the Dirac points. The apparent easy-plane anisotropy in CrCl_3 is identified as the magnetic shape anisotropy

of the dipole-dipole interaction that barely overcomes the weak spin-orbit coupling of light Cl^- ligand ions [35]. Whereas the interlayer exchanges may greatly enhance as the stacking changes down to bilayers [16, 36], the bulk bands in CrCl_3 will exhibit nearly 2D magnons owing to its remarkably weak interlayer couplings.

In this work using inelastic neutron scattering, we report the powder-averaged spin wave excitation spectrum of CrCl_3 and show that its magnon at the Dirac wave vector is indeed gapless and well-described by the 2D spin Hamiltonian including isotropic Heisenberg exchanges only. By comparing the results with the powder-averaged spectrum of CrI_3 , we also find that the magnons in CrCl_3 do not exhibit broadening in energy, which is in remarkable contrast to other van der Waals honeycomb ferromagnets.

2. Methods

The samples used in this study were prepared in a few different forms. The CrCl_3 sample used for inelastic neutron scattering measurements was commercially purchased from Alfa Aesar in polycrystalline form with 99.9% purity. For dc magnetization measurements, the commercial CrCl_3 was recrystallized into relatively larger platelets using the chemical vapor transport method [33]. The CrI_3 samples were initially obtained from batches of crystal growth, for which we used the chemical vapor transport method using I_2 as the transport agent [40]. Two CrI_3 samples were then prepared with relatively large (L) or small (S) grain sizes, respectively. The sample L consisted of small crystallites of approximately 1 mm in width which were collected as-is directly from the growth batch without further treatment. In contrast, the sample S was pulverized by milling with alumina balls overnight. The typical size of the pulverized grains was at sub-micrometer level when viewed under an optical microscope. Both types of CrI_3 samples were used for inelastic neutron scattering and dc magnetization measurements. In the supplemental information (available online at stacks.iop.org/2DM/9/015006/mmedia), we show the comparison of the elastic parts of the neutron scattering data between the two CrI_3 samples confirming that the Bragg peaks in the sample S are significantly broader than those in the sample L [41]. We also observe a consistent difference in the x-ray diffraction data collected at room temperature [41].

Our inelastic neutron scattering experiments were performed using two time-of-flight spectrometers at the Spallation Neutron Source, Oak Ridge National Laboratory. Spin wave excitations of CrCl_3 were measured on the SEQUOIA spectrometer using incident neutron energies of $E_i = 25, 12$, or 4 meV [37]. We used ~ 1 g sample containing a large number of randomly oriented polycrystalline pieces of CrCl_3 , which were sealed in an aluminum can with helium

for thermal exchange. The excitations of the two CrI_3 samples were measured on the HYSPEC spectrometer using an incident neutron energy of $E_i = 25$ meV [38]. The sample mass is ~ 6 g for both L and S samples, respectively.

To analyze the inelastic neutrons scattering intensities, we calculated the neutron scattering cross section of the magnon excitations using the SpinW program [39]. The magnon calculation was based on the linear spin wave approximation within the Holstein-Primakoff formalism. The least square fitting was performed between the observed and calculated intensities over the same wave vector ranges, from which we obtained the best-fit exchange constants. The model spin Hamiltonian and the parameters included will be discussed in the next section.

3. Results and discussions

3.1. DC magnetization

We first discuss the dc magnetization data of CrCl_3 and two different CrI_3 crystalline samples, which are summarized in figure 2. The measurements were done with dc magnetic field applied along the c axis taking advantage of the distinctive platelike shape of the van der Waals crystals. We note, however, that the orientations of the CrI_3 -S platelets were relatively uncertain.

In CrCl_3 , the antiferromagnetic transition is easily noticed as a sharp kink at $T_N = 14.0$ K in the temperature dependent magnetization (M/H) plotted in figure 2(a). Since its inverse magnetization deviated significantly from linearity, the ferromagnetic transition could not be identified by fitting with the Curie-Weiss law. The Curie temperature of CrCl_3 has previously been identified at $T_C = 17.2$ K by heat capacity measurement [33]. In our current dc magnetization data, we find that the maximum of its second derivative, $d^2(M/H)/dT^2$, is located at the same temperature (see figure 2(a), right axis). We consider it to be the better estimate of T_C than the maximum of the first derivative, which is located at a lower temperature by ~ 2 K [36].

The field dependence of the magnetization of CrCl_3 is plotted in figure 2(b) as m - H hysteresis curves, where m is the magnetic moment per Cr ion. Three temperatures are selected to represent the paramagnetic ($T = 50$ K), ferromagnetic ($T = 14$ K), and antiferromagnetic ($T = 3$ K) phases, respectively. Whereas the magnetic moment in the paramagnetic phase changes weakly over the entire range below 10 kOe, in the antiferromagnetic phase exhibits a sharp change in the slope at around 5.6 kOe followed by gradual saturation to the value of $m \approx 3\mu_B$. In the intermediate and ferromagnetic phase, the magnetic moment does not linearly depend on the magnetic field. The inset in figure 2(b) shows there are small but finite remnant magnetizations, $\sim 0.014\mu_B$, which are nearly identical between the two phases. It thus

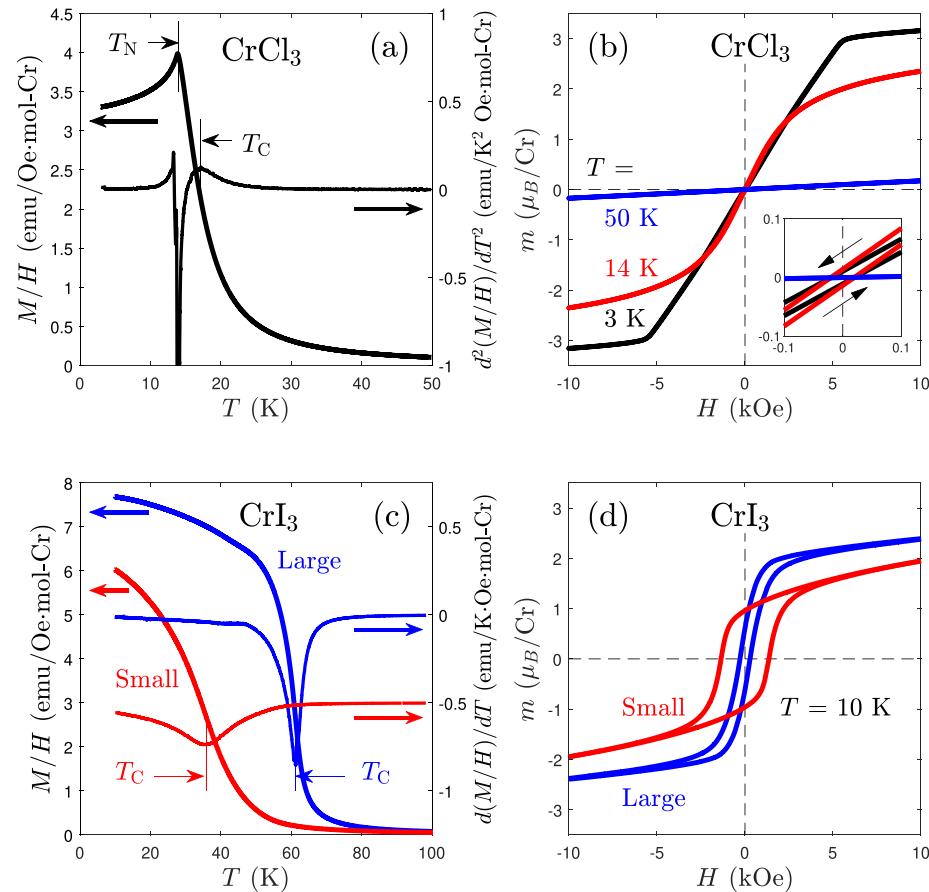


Figure 2. (a) Temperature dependence of the dc magnetization, $M(T)/H$, and its second derivative, $d^2(M(T)/H)/dT^2$ (thin lines and right axis), of CrCl_3 with an external field $H = 1\text{ kOe}$ applied along the c axis. (b) The magnetic hysteresis curves of CrCl_3 at selected temperatures with external magnetic field along the c axis. The inset shows the data around zero field. (c) Temperature dependencies of the dc magnetization, $M(T)/H$, and their derivatives, $d(M(T)/H)/dT$ (thin lines and right axis), of the large and small powder samples of CrI_3 , respectively. The derivative for the small sample is vertically shifted for clarity. (d) The magnetic hysteresis curves of the large and small powder samples of CrI_3 at $T = 10\text{ K}$.

suggests that the ferromagnetic orderings within van der Waals monolayers remain unchanged below T_C .

The temperature dependences of dc magnetization of the two CrI_3 samples, L and S, are plotted in figure 2(c). While both samples show expected transitions from paramagnetic to ferromagnetic, T_C is noticeably smaller in the sample S which was pulverized with ball milling. Contrary to the case of CrCl_3 , in CrI_3 -L we find the maximum of its first derivative is located closer to the previously known Curie temperature at $T_C = 61.3\text{ K}$ than the second derivative. We thus use the same method to identify the Curie temperature of CrCl_3 -S at $T_C = 35.8\text{ K}$. Note that this is quite close to the Curie temperature of CrI_3 in the monolayer limits [3]. Therefore, we conclude that the effect of ball-milling was to significantly reduce not only the area of van der Waals layers but also the number of stacked layers.

Another evidence for effective thinning of the sample S is found in the enhanced coercivity revealed in the $m-H$ hysteresis curves. As plotted in figure 2(d), the sample S has significantly larger coercive field ($H_c^S \approx 1.3\text{ kOe}$) than the sample L at 0.30 kOe although the former has smaller moment

in zero field. This behavior is consistent not only with the previous independent observations of the bulk and monolayer samples [3, 40], but also the recent report of surface layers being harder than the bulk by the magnetic force microscopy measurements [42]. Therefore, we conclude that the sample S is closer to the monolayer limits than the sample L.

3.2. Spin wave excitations in CrCl_3

Overview of the inelastic neutron scattering intensities of CrCl_3 at $T = 4\text{ K}$ is displayed in figure 1(d). Strong and dispersive excitations are observed at low energies below $E \leq 9\text{ meV}$, whose intensity decreases at larger wave vectors (Q) indicating that these are magnetic excitations. These excitations consist of two bands separated at $\sim 4\text{ meV}$, which are ascribed to the two sublattice spins of a simple honeycomb lattice. The upper and lower bands account for in-phase and out-of-phase precessions, respectively, of the two sublattice spins. Additional intensities observed at high energies, $E \approx 14.5$ and 17.5 meV , are ascribed to phonon excitations as they increase in intensity at higher wave vectors. These energies are also consistent

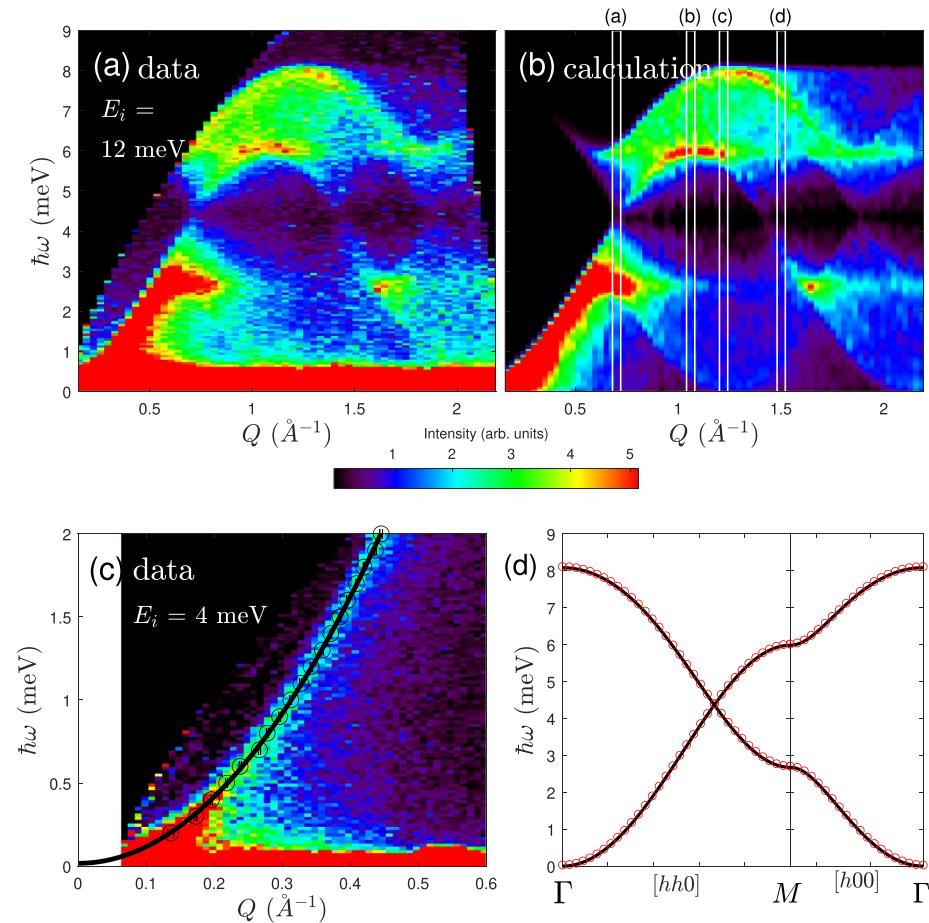


Figure 3. (a) The powder-averaged spin wave excitation intensities of CrCl_3 measured at $T = 4 \text{ K}$ with $E_i = 12 \text{ meV}$ and (b) the calculated intensities convoluted with the instrumental resolution. The best-fit values of J_1, J_2 and J_3 used in (b) are listed in the main text. The double vertical lines and the alphabets above them mark the ranges of integration for constant- Q plots in figure 4 and the corresponding subplot labels, respectively. (c) The low-energy part of the spin wave excitations measured with $E_i = 4 \text{ meV}$. The black solid line is the quadratic fit to the peak positions marked with open circles. (d) Calculated spin wave energies along selected high-symmetry directions. The solid lines are the calculations using J_1, J_2 and J_3 only while the red circles also include $J_c = 0.0077 \text{ meV}$ and $D = 0.014 \text{ meV}$.

with recent Raman scattering observations of phonon signals at ~ 115 and 140 cm^{-1} [1, 16].

To observe the details of spin wave excitations, we repeated the measurements with instrumental setups providing higher energy resolutions. First, the data obtained with the incident energy at $E_i = 12 \text{ meV}$ is shown in figure 3(a). The upper band includes two distinctive intensity maxima due to powder averaging: one near $E \approx 6 \text{ meV}$ and the other 8 meV . The maximum at 6 meV corresponds to the van Hove singularity at $Q_M = (\frac{1}{2}, \frac{1}{2}, 0)$ while the other at 8 meV corresponds to the top of the magnon excitation at $Q_\Gamma = (1, 0, 0)$. These two wave vectors are located at the boundary and the center, respectively, of the 2D Brillouin zone of the honeycomb lattice. The overall band structure is consistent with the nearest neighbor exchange (J_1) being ferromagnetic just as in CrBr_3 and CrI_3 . Given the antiferromagnetic coupling between the adjacent ferromagnetic layers and the number of layers per unit cell being three, the dispersion minimum along the c axis is expected to

appear at $Q_Z = (0, 0, \frac{3}{2})$, or $|Q_Z| = 0.54 \text{ \AA}^{-1}$. At the same time, the zero wave vector at $Q=0$ will correspond to the maximum of the dispersion along the c axis which is determined by the strengths of J_c and the magnetic anisotropy. The plots in figure 3(c) shows the low-energy magnon mode around $Q=0$ measured with the incident energy at $E_i = 4 \text{ meV}$ with the full-width-half-maximum energy resolution of 0.09 meV at the elastic channel. We attempted to estimate the dispersion maximum at $Q=0$ by fitting these magnon energies with a typical quadratic function of momentum, $\hbar\omega = aQ^2 + \Delta$. As plotted with a solid line in figure 3(c), the intercept is found at $\Delta = 0.016 \text{ meV}$ which is several times smaller than the instrumental resolution. We thus tentatively conclude that the strengths of J_c and the magnetic anisotropy are too small to be resolved by the current experimental configurations.

To fit the spin wave spectrum and extract the exchange constants, we consider the spin Hamiltonian including three intra-plane (J_1, J_2, J_3) and

Table 1. Comparison of exchange parameters among CrCl_3 , CrBr_3 and CrI_3 . DM is the strength of DM exchange. All units are in meV except the temperatures in K. Note that, for CrI_3 , an updated set of parameters are reported in [6] including additional interplane exchanges that are not shown in figure 1(b) or (c).

	$T_N(\text{K})$	$T_C(\text{K})$	J_1	J_2	J_3	J_c	DM	D	Note
CrCl_3	14.0	17.2	-0.95	-0.024	0.051	0.008 ^a	—	0.014 ^a	This work
CrBr_3	—	32	-1.36	-0.06	0.12	—	0.07	-0.04	[32]
CrI_3	—	61	-2.01	-0.16	0.08	-0.59	0.31	-0.22	[5]

^a Not used for the spin wave calculations.

one inter-plane (J_c) isotropic Heisenberg exchanges depicted in figure 1(a) as well as the easy-plane anisotropy ($D > 0$):

$$H = \frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_j D (\mathbf{S}_j \cdot \hat{\mathbf{z}})^2. \quad (1)$$

Since the observed spectra do not reveal low-lying branches perpendicular to the honeycomb planes, we attempted to estimate the values of J_c and D from the existing magnetization data in the literature. The dc magnetization of bulk CrCl_3 is reported to saturate at $B_{ab}^{sat} = 0.20$ T or $B_c^{sat} = 0.56$ T along the direction parallel or perpendicular to the honeycomb planes, respectively [36, 43]. Given that antiferromagnetic J_c must be overcome to arrive at the in-plane saturation, we obtain $J_c = g\mu_B B_{ab}^{sat}/2S = 0.0077$ meV where we used $g = 2$ and $S = 3/2$. As both J_c and D must be simultaneously overcome for the out-of-plane saturation, we may subsequently obtain $D = g\mu_B B_c^{sat}/S - J_c = 0.014$ meV. We find that the magnon bandwidth along the $[0\ 0\ L]$ direction becomes as small as 0.03 meV when these two parameters are included. The in-plane dispersions with and without them, respectively, are plotted in figure 3(d). For this reason, we included only the three in-plane Heisenberg exchanges to perform least square fittings of the linear spin wave intensities against the inelastic neutron scattering data. The resultant best fit parameters are $J_1 = -0.95$ meV, $J_2 = -0.024$ meV, and $J_3 = 0.051$ meV, and the calculations using these parameters are shown in figure 3(b). The values of these parameters are also listed in table 1 along with those previously reported for CrBr_3 and CrI_3 .

Since large topological energy gaps have been observed in the magnon bands of CrI_3 and CrBr_3 [5, 6, 32], it is important to check whether or not such gaps appear also at the Dirac points of CrCl_3 . Although the excitation spectrum in figure 3(a) is powder-averaged, its Dirac point at $|\mathbf{Q}_{\frac{1}{3}\frac{1}{3}0}| = 0.70 \text{ \AA}^{-1}$ is clearly visible at $\hbar\omega = 4.4$ meV. The apparent intensity discontinuity between the upper and lower modes is observed at the wave vector corresponding to the Dirac crossings of the linear dispersions. To check for the possible of a gap opening, we plot a few selected constant- Q cuts of the inelastic neutron scattering intensities including the Dirac wave vector in figure 4. The calculated intensities,

which are convoluted by the instrumental resolutions only, are plotted together as solid lines. The excellent agreement between the observations and calculations indicates that there is no additional broadening in the excitation. Such behavior is in remarkable contrast to the excitation spectra of CrI_3 or CrBr_3 , which exhibit significant broadening in energy throughout their magnon bands at low temperatures [5, 6, 32]. The magnon broadening in insulating ferromagnets typically occurs via magnon-magnon interactions or magnon-phonon coupling as the temperature approaches T_C [44–46]. We thus stress that the resolution-limited magnon in CrCl_3 at $T = 4$ K is considered normal whereas the magnon broadening observed in CrI_3 and CrBr_3 are anomalous. Since the magnon broadening in these van der Waals ferromagnets is beyond the scope of the current work, this subject will be investigated in a separate work. Taking this into account, we find that the constant energy cut at $|\mathbf{Q}_{\frac{1}{3}\frac{1}{3}0}| = 0.70 \text{ \AA}^{-1}$ is well explained by a calculation without a gap opening contrary to CrI_3 and CrBr_3 . The absence of the Dirac gap in CrCl_3 is consistent with its spins being oriented parallel to the honeycomb plane in zero field. Note that the gap openings in CrI_3 and CrBr_3 are ascribed to the DM vectors oriented perpendicular to the honeycomb planes and parallel to the ordered spins [5, 32].

3.3. Spin wave excitations in CrI_3

We have just shown in CrCl_3 that the ratio of its net inter-planar to net intra-planar exchanges per Cr^{3+} spin is 3×10^{-3} . This ratio is a few orders of magnitude smaller than $\sim 9 \times 10^{-1}$ in CrI_3 [5, 6]. Since spin wave energies of CrCl_3 will hardly change upon inclusions of the inter-planar exchanges, the excitations observed in this work must be virtually identical to the magnons in the monolayer limit. In the case of CrI_3 , 2D magnon energies have been observed by means of Raman scattering in the monolayer limit [47]. These energies are largely consistent with those of the bulk crystals when the interplanar exchanges are excluded. To observe magnon energies in CrI_3 close to the 2D limit, we performed inelastic neutron scattering measurements on the two polycrystalline samples with different amounts of thinning. As previously described, the sample S is mechanically reduced down close to the 2D limit. The momentum-integrated neutron scattering intensities

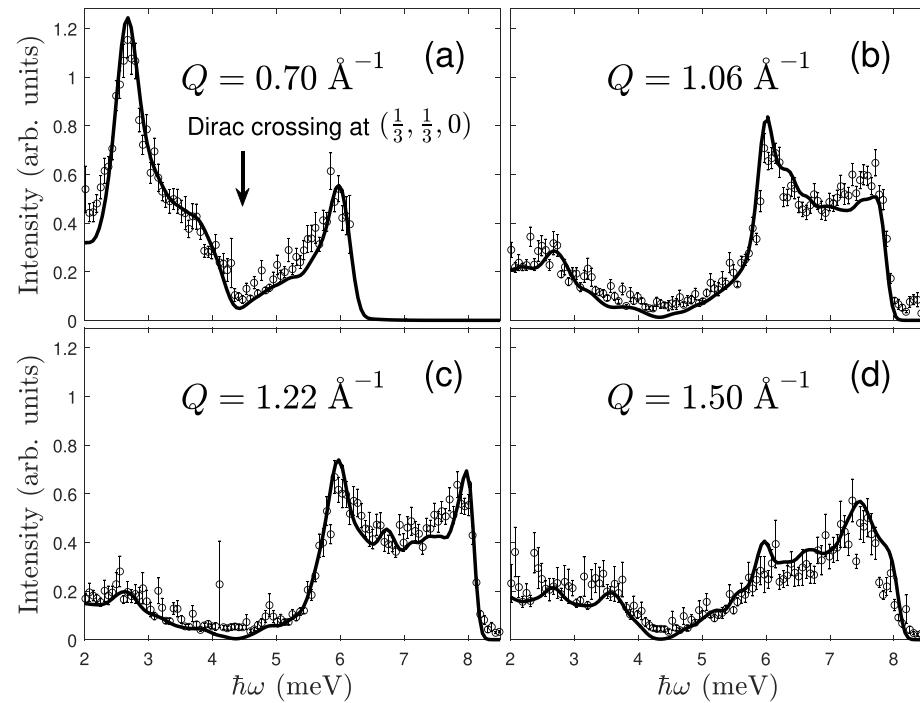


Figure 4. Energy dependencies of the spin wave excitation intensities at momentum transfer values (Q). The ranges of integration are marked as double vertical lines in figure 3(b). The open circles are the inelastic neutron scattering data measured with $E_i = 12$ meV, which are integrated over $\pm 0.02 \text{ \AA}^{-1}$. The solid lines are the calculated intensities using the parameters discussed in the text convoluted with the energy-dependent instrumental resolutions.

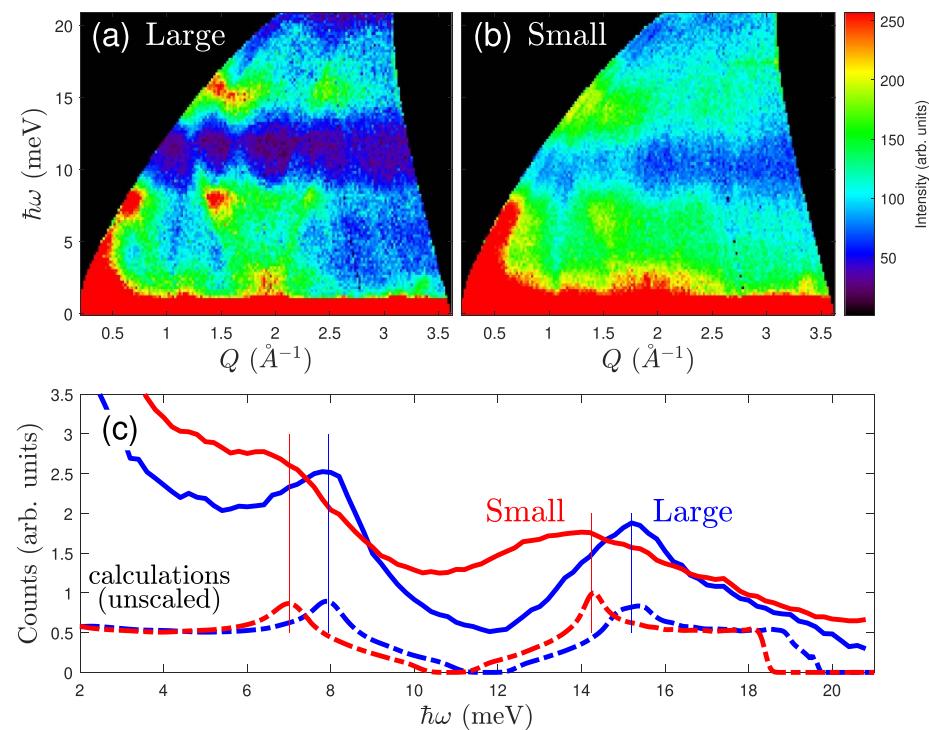


Figure 5. (a), (b) The powder-averaged inelastic neutron scattering intensities of (a) L and (b) S samples of CrI_3 measured at $T = 2$ K with $E_i = 25$ meV. (c) Energy dependences of the Q -integrated inelastic neutron scattering intensities. Solid lines are the experimental data while dashed lines are the calculated intensities using the parameters reported in [6]. Note that the latter was convoluted with the energy-dependent instrumental resolutions.

of the sample L and S, respectively, at $T = 2$ K are plotted in figure 5. Commonly in both samples, the powder-averaged excitation spectra exhibit two

distinct bands corresponding to the upper and lower magnon modes, respectively, expected for honeycomb ferromagnets. Their overall band structures are

equivalent to that of CrCl_3 (see figure 3) although the excitations in the sample S are significantly broader in energy. It thus suggests that CrI_3 still retains its in-plane honeycomb structure after the ball milling.

When we directly compare the integrated magnon densities of states, it becomes clear that the two intensity peaks of the sample S are shifted to lower energy by ~ 1 meV. To understand the origin of the observed energy shift, we performed the linear spin wave calculations based on the spin Hamiltonian derived recently from the single crystal excitations. In figure 5(c), the blue dash-dotted line is calculated using the exact three dimensional spin Hamiltonian reported in [6] while the red dash-dotted line is the 2D calculation excluding the inter-planar exchanges. We note that both lines were convoluted with the energy-dependent instrumental resolutions. Remarkably, the two maxima of the 2D calculation excellently match those of the sample S. Such agreement strongly suggests that the ordered stacking of the van der Waals layers in this sample is effectively compromised resulting in nearly 2D magnetism. It also confirms that the bulk excitations of CrI_3 are far from 2D magnons. We also note that spectra of both samples are significantly broader than the instrumental resolutions. Such behavior is consistent with the broadening already observed in the bulk crystal excitations, and is thus most likely intrinsic to the CrI_3 .

4. Conclusions

In this work, we used inelastic neutron scattering to study powder-averaged magnon excitations in the van der Waals honeycomb ferromagnets CrCl_3 and CrI_3 . While their magnon band structures were qualitatively equivalent, we found that magnons in CrCl_3 did not exhibit broadening in energy contrary to CrI_3 where significant broadening was observed. The magnon excitation spectrum of CrCl_3 could be reproduced using the 2D spin Hamiltonian including in-plane Heisenberg exchange only and without considering the energy gap opening at the Dirac point, which are also in contrast to CrI_3 . Based on these observations, we conclude that the 2D Dirac magnon in CrCl_3 is massless and not topological.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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