Evidence of the polaronic character of excitons in a two-dimensional semiconducting magnet CrI$_3$

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Abstract

Studies of exciton dynamics in two-dimensional (2D) transition metal dichalcogenide (TMDC) semiconductors have led to discoveries of a variety of fascinating properties for optoelectronic applications [1]. It has been known that exciton dynamics can be strongly affected by lattice vibrations through electron-phonon (e-ph) coupling, which can be described by the formation of exciton-polarons [2] – composite quasiparticles with excitons dressed by a cloud of polar phonons. The recently discovered 2D magnetic semiconductor, CrI₃, provides a new platform to explore exciton physics beyond the well-studied 2D TMDC semiconductors because of its localized orbitals [3] and intrinsic long-range magnetic order [4]. However, the nature of excitons as well as the roles of magnetic ordering and e-ph coupling in the exciton dynamics remain elusive in 2D CrI₃. Here in bilayer CrI₃, we first performed temperature-dependent photoluminescence and linear absorption measurements to show the presence of strong e-ph coupling. We then carried out careful temperature and magnetic field-dependent resonant micro-Raman spectroscopy measurements and discovered a rare Raman feature of periodic broad modes up to as high as the 8th order, providing direct evidence of the polaronic character of excitons. We establish that the formation of polarons in CrI₃ is dominated by the strong Fröhlich interactions between the bright exciton at ~1.96 eV and a longitudinal optical phonon at 120 cm⁻¹. We further show that the emergence of long-range magnetic order below $T_C = 45$ K enhances the e-ph coupling and that the transition from layered antiferromagnetic to ferromagnetic order across $B_C = 0.7$ T tunes the polaron spectra, suggesting a strong coupling among the lattice, charge and spin degrees of freedom in 2D CrI₃. Our study opens up new avenues for tailoring light-matter interactions in 2D semiconductors with long-range orders and strong correlations.

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The polaronic effect, which describes the strong coupling between charge and lattice vibrations, plays a key role in a broad class of novel quantum phenomena ranging from colossal magnetoresistance [5] to anomalous photovoltaic effect [6]. In particular, the polaronic effect on excitons can profoundly modulate exciton dynamics upon photoexcitation and has been employed to describe intriguing optical and optoelectronic properties in materials such as hybrid organic-inorganic perovskite solar cells [7–9]. Compared to three-dimensional (3D) bulk systems, two-dimensional (2D) atomic crystals possess a couple of unique advantages in exploring the polaronic effect on exciton dynamics. First, the reduced dielectric screening in atomically thin samples enhances both the excitonic effect [1] and the electron-phonon (e-ph) coupling [10], which is expected to promote the formation of exciton-polarons. Second, unlike bulk materials in which the e-ph coupling is largely determined by intrinsic electronic and phonon band structures with limited tunability, 2D materials provide greater flexibility for engineering e-ph coupling through a battery of approaches including carrier doping [11, 12] and interfacial coupling [13–17], as well as dimensionality modulation [10], and so hold high promise for the future development of optoelectronic devices.

The realization of a long-range magnetic order in 2D semiconducting CrI$_3$ opens new pathways to engineer optical and optoelectronic properties of 2D semiconductors tunable with magnetic field [18–27]. On the one hand, the large excitonic effect [28] from the localized molecular orbitals can be considered as the microscopic origin of the giant magneto-optical Kerr effect [4] and magnetic circular dichroism [3] signals in 2D CrI$_3$. On the other hand, the strong e-ph coupling is interpreted to cause the large Stokes shift, profound broadness, and skewed lineshape in the photoluminescence (PL) spectra of 2D CrI$_3$ [3]. While it is not surprising then to expect excitons strongly coupling to phonons to develop exciton-polarons in 2D CrI$_3$, this has not yet been investigated experimentally. Additionally, 2D CrI$_3$ also provides the unprecedented opportunity to explore the role of the long-range magnetic order on exciton-polarons, as well as the interplay among the lattice, charge, and spin degrees of freedom (DoFs), all of which are untouched territories in 2D materials research thus far.

One fingerprint for polaron formation is the development of phonon-dressed electronic bands that appear as satellite bands in proximity to the original undressed one. Such features manifest as multiple equally spaced replica bands in angle-resolved photoemission spectroscopy (ARPES) [16, 29–34] or as discrete absorption and emission lines in linear optical spectroscopy [35].
However, such signatures of exciton-polarons have not been revealed so far in 2D CrI$_3$, as the sizable bandgap ($\sim 1.1$ eV) \cite{3} and extreme surface sensitivity \cite{36} of CrI$_3$ make ARPES measurement challenging while the potential inhomogeneous broadening could largely smear out individual lines for phonon-dressed bands in linear optical spectroscopy. Here, we exploit resonant micro-Raman spectroscopy, a second order nonlinear inelastic optical process, to show the first direct evidence of the polaronic character of excitons in bilayer CrI$_3$, which manifests as a well-defined, broad periodic pattern in the Raman shift frequency that is resolved in addition to sharp phonon peaks. The profile of this periodic pattern and its temperature and magnetic field dependence reveal essential information, including the e-ph coupling strength and the coupling between exciton-polarons and magnetism in bilayer CrI$_3$.

We start by identifying excitonic transitions and e-ph coupling in bilayer CrI$_3$ using temperature dependent PL and linear absorption spectroscopy. Bilayer CrI$_3$ was fully encapsulated between few-layer hexagonal boron nitride (hBN) and placed on a sapphire substrate (see Methods). Photoluminescence and linear absorption spectroscopy measurements were then performed in a transmission geometry (see Methods). Figure 1 shows PL and absorbance spectra taken at 80 K, 40 K, and 10 K that are well above, slightly below, and well below the magnetic critical temperature $T_C = 45$ K, respectively \cite{3, 4, 37}. A single PL mode at 1.11 eV and three prominent absorbance peaks at 1.51 eV, 2.00 eV, and 2.68 eV (denoted as A, B, and C, respectively) are observed across the entire temperature range. These three energies are in good agreement with the ligand-field electronic transitions assigned by differential reflectance measurements on monolayer CrI$_3$ \cite{3} and bulk CrI$_3$ \cite{38-40}, and have been later revealed to be bright exciton states through more recent sophisticated first principle GW and Bethe-Salpeter equation (GW-BSE) calculations \cite{28}. While the absorbance spectra show little temperature dependence except the appearance of a weak shoulder at 1.79 eV at 10 K (orange arrow), the PL spectra are clearly temperature dependent. The temperature dependence of the PL full width at half maximum (FWHM), $\Gamma(T)$, is well fitted by the model functional form, $\Gamma(T) = \Gamma_0 + \frac{\gamma}{\exp\left(\frac{\hbar \omega_{LO}}{k_B T} \right) - 1}$, with the first term for temperature-independent inhomogeneous broadening and the second term for homogeneous broadening from exciton coupled with a LO phonon at frequency $\omega_{LO}$. Taking $\omega_{LO} = 120.6$ cm$^{-1}$ found later on in Fig. 2, we obtain $\Gamma_0 = 163.9 \pm 2.7$ meV and $\gamma = 164.2 \pm 8.1$ meV, which suggests that the broadness of the exciton modes arises from both inhomogeneous broadening from impurities or disorders and e-ph coupling.
We next proceed to perform resonant micro-Raman spectroscopy measurements with an incident wavelength of 633 nm (1.96 eV) matching the energy of the B exciton on an encapsulated bilayer CrI$_3$ flake placed on a SiO$_2$/Si substrate (see Methods). Figure 2a displays a representative Raman spectrum acquired in the crossed linear polarization channel at 70 K (above $T_C = 45$ K). We note that this spectrum covers a much wider frequency range than earlier Raman studies on CrI$_3$ [36, 37, 41, 42]. The first-order single phonon peaks appear in the relatively low frequency range of 70 – 140 cm$^{-1}$, and are assigned to be of either $A_g$ or $E_g$ symmetries under the $C_{3i}$ point group (labeled as $A_{1-3}$ and $E_{1-4}$ in the inset of Fig. 2a) which is consistent with earlier work [36, 37, 41, 42]. The second-order two-phonon modes show up in a slightly higher frequency range of 180 – 280 cm$^{-1}$, and have much weaker intensities and broader linewidths as expected (see Supplementary Section 1). In addition to these phonon features, we resolve a remarkable periodic modulation across a wide frequency range of 70 – 800 cm$^{-1}$ in the low intensity part of the Raman spectrum. This is highlighted by the orange shaded area in Fig. 2a and magnified in Fig. 2b. Similar features can be reproduced in 2D CrI$_3$ of other thicknesses with only subtle quantitative variations (see Supplementary Section 2). We clearly see in Fig. 2a and 2b that the first- and second-order phonon modes have much narrower linewidths than the modulation feature, which rules out the possibility of this periodic pattern being from higher-order multiple-phonon processes.

To better understand the origin of the periodic pattern in the bilayer CrI$_3$ Raman spectrum, we fit the pattern using a summation of Lorentzian profiles of the form $\sum_N \frac{A_N (\Gamma_N/2)^2}{(\omega - \omega_N)^2 + (\Gamma_N/2)^2}$ with central frequency $\omega_N$, linewidth $\Gamma_N$, and peak intensity $A_N$ of the $N^{th}$ period. Figure 2c shows the plot of the central frequency $\Gamma_N$ as a function of $N$, from which a linear regression fit gives a periodicity of 120.6 ± 0.9 cm$^{-1}$ and an interception of 0 ± 0.2 cm$^{-1}$ (see Supplementary Section 3 for the 0$^{th}$ broad mode). Figure 2d reveals a monotonically increasing trend for the line width $\Gamma_N$, with ~ 63 cm$^{-1}$ for $N = 1$ up to ~ 110 cm$^{-1}$ for $N = 6$. Such an extremely broad and precisely periodic feature in CrI$_3$ is in clear contrast to the cascade multiphonon overtones previously reported in Eu, Cd, Yb monochalcogenides [43-50] from three aspects: the much broader linewidth than that of phonons, the absence of the LO phonon at $\omega_{LO} = 120.6$ cm$^{-1}$ in the first-order phonon Raman spectra (Fig. 2a inset), and the Poisson distribution, instead of the exponential decay, for $A_N$ (Fig. 3c) (see Supplementary Section 4). Meanwhile, strikingly similar features have been
seen in polaron systems through the energy dispersion curves of ARPES [16, 29–34], as well as through linear absorption and PL spectroscopy [8, 51]. In those cases, the periodic patterns in their energy spectra were determined as the phonon-dressed electronic state replicas induced by the polaronic effect, or sometimes also referred as phonon-Floquet states [52], and the periodicity is given by the frequency of phonons participating in the formation of the polarons. Due to the high resemblance between the lineshapes of our Raman spectrum and those polaron energy spectra [8, 16, 29–34, 51], as well as the large e-ph coupling strength present in CrI$_3$ [3], we assign that the broad periodic feature seen here stems to polaronic origins, whereby the B exciton at 1.96 eV, with the electron (hole) in the weakly dispersive conduction (highly dispersive valence) band of Cr 3$d$ (1 $5p$) orbital character [28, 53], couples strongly to a phonon at 120 cm$^{-1}$ [54]. Because the phonon mode involved in the formation of the polarons are parity odd [55], it is expected to be Raman inactive for a centrosymmetric crystal, which is consistent with the absence of 120 cm$^{-1}$ phonon mode in the Raman phonon spectra.

We then proceed to identify the source and the character of the phonon at 120 cm$^{-1}$. We first rule out the possibility of this phonon arising from either the hBN encapsulation layers or the SiO$_2$/Si substrate, as a similar periodic pattern in the Raman spectrum is also observed in bare bulk CrI$_3$ crystals (see Supplementary Section 5). We then propose the longitudinal optical (LO) phonon calculated at $\sim$115 cm$^{-1}$ from the phonon band dispersion in monolayer CrI$_3$ [56] as a promising candidate, whose slight energy difference from the experimental value of 120 cm$^{-1}$ could result from calculation uncertainties. This LO phonon mode belongs to the $E_u$ symmetry of the $C_{3i}$ point group, and its atomic displacement induces an in-plane polar moment [56]. Consequently, an electric field is generated upon the activation of this LO phonon and interacts strongly with the B excitons through the Coulomb interactions, thus promoting the formation of exciton-polarons in bilayer CrI$_3$. Furthermore, this LO phonon band at $\sim$115 cm$^{-1}$ is nearly dispersionless, and so is expected to have a large density of states, increasing its potential for coupling with the excitons in bilayer CrI$_3$.

It has been shown theoretically that the polaron system consisting of dispersionless LO phonons and charges is one of the few exactly solvable models in many-body physics [57]. The calculated polaron spectra can be well-described by a Frank-Condon model with a Poisson distribution function, $A_N = A_0 e^{-\alpha^N / N!}$ [58, 59], where $A_0$ is the peak intensity of the original electronic band, $A_N$ is
the peak intensity for the $N^{th}$ replica band with $N$ phonon(s) dressed, and $\alpha$ is a constant related to the e-ph coupling in 3D (i.e., $\alpha_{3D}$) that can be scaled by a factor of $3\pi/4$ for 2D (i.e., $\alpha_{2D}$) \cite{60}. Based on this model, we proceed to fit with the Poisson distribution function the Lorentzian peak intensity profile extracted from Fig. 2b and arrive at $\alpha_{3D} = 2.4$ (scaled to $\alpha_{2D} = 1.0$) at 70 K in bilayer CrI$_3$. This value of $\alpha_{2D}$ is comparable to that for other 2D polaron systems including graphene/hBN heterostructures ($\alpha_{2D} = 0.9$) \cite{16} and bare SrTiO$_3$ surfaces ($\alpha_{2D} = 1.1$) \cite{31}, which positions bilayer CrI$_3$ within the intermediate e-ph coupling regime and confirms the formation of 2D Fröhlich exciton-polarons in this system. The noticeably higher visibility of high-order replica bands in bilayer CrI$_3$ (up to $N = 6$ at 70 K) possibly results from a combination of the narrow exciton linewidth ($\sim 60$ cm$^{-1}$) and the dispersion-less LO phonon frequency ($\sim 120$ cm$^{-1}$). Despite the general success of the Frank-Condon model in describing 2D Fröhlich polarons in the aforementioned systems \cite{30, 31, 33, 34}, a more detailed and accurate microscopic model, especially with the exciton effect accounted for, is highly desired for understanding the formation and consequences of 2D Fröhlich exciton-polarons in bilayer CrI$_3$.

Given the coexistence of a 2D long-range magnetic order and 2D Fröhlich exciton-polarons below $T_C = 45$ K in bilayer CrI$_3$, it is natural to explore the interplay between the two. For this, we have performed careful temperature-dependent polaron Raman spectroscopy measurements and fitted the periodic pattern in every polaron spectrum with a sum of Lorentzian profiles. Figure 3a and 3b displays the polaron Raman spectra taken at 40 K and 10 K, slightly and well below $T_C$, respectively. Compared with the spectrum at 70 K (Fig. 2b), not only do more high-order replica bands become visible at lower temperatures (i.e., up to $N = 8$ at 10 K), but also the spectral weight shifts towards the higher-order bands (i.e., from $N = 1$ at 70 K to between $N = 3$ and 4 at 10 K in Fig. 3c). By fitting the Lorentzian peak intensity profile at every temperature to a Poisson distribution function, we extracted the temperature dependence of $\alpha_{2D}$. As shown in Fig. 3d, $\alpha_{2D}$ remains nearly constant until the system is cooled to $T_C$ and then increases by nearly 50% at the lowest available temperature of 10 K. The observation that $\alpha_{2D}$ enhances anomalously below the magnetic onset $T_C$ suggests an appreciable coupling among the spin, charge, and lattice DoFs in bilayer CrI$_3$. This provides a new material platform of atomic crystals for exploring strong entanglements among multiple DoFs in the 2D limit, in addition to complex transition metal oxides interfaces \cite{31-34}. 


It is known that bilayer CrI\textsubscript{3} transitions from a layered antiferromagnet (AFM) to ferromagnet (FM) with increasing out-of-plane magnetic field ($B_\perp$) above the critical value of $B_C \sim \pm 0.7$ T \cite{3,4,19,21}. We then finally explore the 2D Fröhlich exciton-polaron evolution across this magnetic phase transition by performing magnetic field-dependent polaron Raman spectroscopy measurements. Different from the linear polarizations used in the magnetic field free Raman measurements above, we chose circularly polarized light to perform magnetic field-dependent measurements here in order to eliminate any Faraday effect from the optical components that are situated within the strong magnetic field. Figure 4a shows polaron Raman spectra taken at $B_\perp = 0$ T and $\pm 1$ T, below and above $B_C$, respectively, in both RR and LL channels, where RR(LL) is for the polarization channel selecting the right-hand (left-hand) circular polarization for both incident and scattered light (see Supplementary Section 6). At 0 T, the polaron spectra are the same in RR and LL channels, consistent with zero net magnetization in the layered AFM state for bilayer CrI\textsubscript{3} at $B_\perp < B_C$. At $\pm 1$ T, the polaron spectra in RR and LL channels show opposite relative intensities under opposite magnetic field directions, determined by the net magnetization, aligned along the $B_\perp$ direction, in the FM state for bilayer CrI\textsubscript{3} at $B_\perp > B_C$. To better quantify the magnetic field dependence of the polaron spectra, without loss of the generality, we measured polaron Raman spectra in RR channel at $B_\perp$ from 0 T to 1.4 T every 0.1 T. We fit the spectrum at every magnetic field to extract $A_N$, $A_0$, and $\alpha_{2D}$. Figure 4b shows that the Lorentzian peak intensity profiles segregate into two groups, one for $B_\perp = 0 - 0.7$ T and the other for $0.8 - 1.4$ T, coinciding with the first-order magnetic phase transition at $B_C \sim 0.7$ T. Specifically, Figure 4c shows that $A_0$ has an abrupt decrease at $B_C \sim 0.7$ T and $\alpha_{2D}$ remains nearly constant over the magnetic field range from 0 T to 1.4 T. The suppression(increase) of $A_0$ above(below) $B_C \sim \pm 0.7(-0.7)$ T in RR(LL) channel results from both the development of a net magnetization and the restoration of spatial inversion symmetry across $B_C$ \cite{61,62}. The magnetic field independence of $\alpha_{2D}$ reveals that it is the intralayer, rather than interlayer, magnetism coupled to the 2D exciton-polarons in bilayer CrI\textsubscript{3}.

Our data and analysis reveal the existence of 2D exciton-polarons in bilayer CrI\textsubscript{3} which arises from the strong coupling between the lattice and charge DoFs and can be dramatically modified by the spin DoF of CrI\textsubscript{3}. The exceptionally high number of phonon-dressed electronic state replicas here suggests 2D CrI\textsubscript{3} as an outstanding platform to explore novel phases out of phonon-Floquet engineering, while the significant coupling to the spin DoF adds an extra flavor whose impact on the phonon-Floquet states has not been studied thus far. For example, one can imagine creating
topological states through the band inversion between the phonon-dressed replicas of CrI$_3$ and the electronic state of a material in close proximity.

**Methods**

**Sample fabrication.** CrI$_3$ single crystals were grown by the chemical vapor transport method, as detailed in Ref. [37]. Bilayer CrI$_3$ samples were exfoliated in a nitrogen-filled glovebox. Using a polymer-stamping transfer technique inside the glove box, bilayer CrI$_3$ flakes were sandwiched between two few-layer hBN flakes and transferred onto SiO$_2$/Si substrates and sapphire substrates for Raman spectroscopy and PL/linear absorption spectroscopy measurements, respectively.

**Linear absorption spectroscopy.** A bilayer CrI$_3$ sample on a sapphire substrate was mounted in a closed-cycle cryostat for the temperature-dependent absorption spectroscopy measurements. A broadband tungsten lamp was focused onto the sample via a $50 \times$ long working distance objective. The transmitted light was collected by another objective and coupled to a spectrometer with a spectral resolution of 0.2 nm. The absorption spectra were determined by $1 - \frac{I_{\text{sample}}(\lambda)}{I_{\text{substrate}}(\lambda)}$, where $I_{\text{sample}}(\lambda)$ and $I_{\text{substrate}}(\lambda)$ were the transmitted intensity through the combination of sample and substrate and through the bare substrate, respectively.

**Photoluminescence spectroscopy.** PL spectra were acquired from the same bilayer CrI$_3$ sample where we carried out linear absorption measurements. The sample was excited by a linearly polarized 633 nm laser focused to a $\sim 2 \mu$m spot. A power of 30$\mu$W was used, which corresponds to a similar fluence reported in the literature ($\sim 10 \mu $W over a $\sim 1 \mu$m-diameter spot) [3]. Transmitted right-handed circularly polarized PL signal was dispersed by a 600 groves/mm, 750 nm blaze grating, and detected by an InGaAs camera.

**Raman spectroscopy.** Resonant micro-Raman spectroscopy measurements were carried out using a 633 nm excitation laser for the data in the main text and 473 nm, 532 nm, and 785 nm excitation laser for data in Supplementary Section 7. The incident beam was focused by a $40 \times$ objective down to $\sim 3 \mu$m in diameter at the sample site, and the power was kept at $\sim 80 \mu$W. The scattered light was collected by the objective in a backscattering geometry, then dispersed by a Horiba Labram HR Raman Evolution Raman spectrometer, and finally detected by a thermo-electric cooled CCD camera. A closed-cycle helium cryostat is interfaced with the micro-Raman
system for the temperature-dependent measurements. All thermal cycles were performed at a base pressure lower than $4 \times 10^{-7}$ mbar. In addition, a cryogen-free magnet is integrated with the low temperature cryostat for the magnetic field-dependent measurements. In this experiment, the magnetic field was applied along the out-of-plane direction and covered a range of $0 - 2.2$ Tesla. In order to avoid the Faraday rotation of linearly polarized light as it transmits through the objective under the magnetic field, we used circularly polarized light to perform the magnetic field-dependent Raman measurements.

**Fitting polaron Raman spectroscopy.** For every sample, we have taken temperature and magnetic field dependent Raman spectra on the hBN/SiO$_2$/Si substrate with the same experimental conditions as that on the CrI$_3$ flakes. The Raman spectra from the substrate, an extremely gradual background with a Si phonon peak at $\sim 525$ cm$^{-1}$, shows no dependence on temperature (over the range of $10 - 70$ K) and magnetic field ($0 - 2.2$ T). To fit the polaron Raman spectra of CrI$_3$ flakes, we follow the routine described below. (I) we fit the Si phonon peak at $\sim 525$ cm$^{-1}$ in both spectra taken on the CrI$_3$ thin flake and the bare substrate to extract the Si peak intensity, $I_{Si}^{sample}$ and $I_{Si}^{substrate}$. (II) we multiply the background spectrum by a factor of $I_{Si}^{sample} / I_{Si}^{substrate}$, which is nearly 1, and then subtract off the factored background from the raw Raman spectrum of sample. (III) we fit the sharp CrI$_3$ phonon peaks with Lorentzian functions and substrate subtract their fitted functions from the background free Raman spectrum from step II. This leads to a clean polaron spectrum with only periodic broad modes. (IV) we fit the clean polaron spectrum from step III with a sum of multiple Lorentzian functions, $\sum N \frac{A_N (\Gamma_N/2)^2}{(\omega - \omega_N)^2 + (\Gamma_N/2)^2}$. For the neatness of the data presentation in Fig. 2 and 3, we only show the fitted line from step IV in the plots.

[1] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, “Excitons in atomically thin transition metal dichalcogenides,” [Reviews of Modern Physics 90, 021001 (2018)]

[2] H. Sumi, “Exciton polarons of molecular crystal model. II. Optical spectra,” Journal of the Physical Society of Japan 38, 825–835 (1975).

[3] K. L. Seyler, D. Zhong, D. R. Klein, S. Gao, X. Zhang, B. Huang, E. Navarro-Moratalla, L. Yang, D. H. Cobden, M. A. McGuire, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, “Ligand-field helical luminescence in a 2D ferromagnetic insulator,” [Nature Physics 14, 277–281 (2018)].
[4] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, “Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit,” Nature 546, 270–273 (2017).

[5] C. Jooss, L. Wu, T. Beetz, R. F. Klie, M. Beleggia, M. A. Schofield, S. Schramm, J. Hoffmann, and Y. Zhu, “Polaron melting and ordering as key mechanisms for colossal resistance effects in manganites,” Proceedings of the National Academy of Sciences 104, 13597 (2007).

[6] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, “Hybrid organic–inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties,” Nature Reviews Materials 1, 15007 (2016).

[7] K. Miyata, D. Meggiolaro, M. T. Trinh, P. P. Joshi, E. Mosconi, S. C. Jones, F. De Angelis, and X.-Y. Zhu, “Large polarons in lead halide perovskites,” Science advances 3, e1701217 (2017).

[8] S. Neutzner, F. Thouin, D. Cortecech, A. Petrozza, C. Silva, and A. R. Srimath Kandada, “Exciton-polaron spectral structures in two-dimensional hybrid lead-halide perovskites,” Physical Review Materials 2, 064605 (2018).

[9] F. Thouin, D. A. Valverde-Chávez, C. Quart, D. Cortecech, I. Bargigia, D. Beljonne, A. Petrozza, C. Silva, and A. R. Srimath Kandada, “Phonon coherences reveal the polaronic character of excitons in two-dimensional lead halide perovskites,” Nature Materials 18, 349–356 (2019).

[10] X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, and K. F. Mak, “Strongly enhanced charge-density-wave order in monolayer NbSe2,” Nature Nanotechnology 10, 765–769 (2015).

[11] M. Kang, S. W. Jung, W. J. Shin, Y. Sohn, S. H. Ryu, T. K. Kim, M. Hoesch, and K. S. Kim, “Holstein polaron in a valley-degenerate two-dimensional semiconductor,” Nature Materials 17, 676–680 (2018).

[12] B. Miller, J. Lindlau, M. Bommert, A. Neumann, H. Yamaguchi, A. Holleitner, A. Högele, and U. Wurstbauer, “Tuning the Fröhlich exciton-phonon scattering in monolayer MoS2,” Nature Communications 10, 807 (2019).

[13] C. Jin, J. Kim, J. Suh, Z. Shi, B. Chen, X. Fan, M. Kam, K. Watanabe, T. Taniguchi, S. Tongay, A. Zettl, J. Wu, and F. Wang, “Interlayer electron-phonon coupling in WSe2/hBN heterostructures,” Nature Physics 13, 127–131 (2017).

[14] C. M. Chow, H. Yu, A. M. Jones, J. Yan, D. G. Mandrus, T. Taniguchi, K. Watanabe, W. Yao, and X. Xu, “Unusual exciton-phonon interactions at van der Waals engineered interfaces,” Nano Letters...
[15] G. S. N. Eliel, M. V. O. Moutinho, A. C. Gadelha, A. Righi, L. C. Campos, H. B. Ribeiro, P.-W. Chiu, K. Watanabe, T. Taniguchi, P. Puech, M. Paillot, T. Michel, P. Venezuela, and M. A. Pimenta, “Intralayer and interlayer electron-phonon interactions in twisted graphene heterostructures,” Nature Communications 9, 1221 (2018).

[16] C. Chen, J. Avila, S. Wang, Y. Wang, M. Mucha-Kruczyński, C. Shen, R. Yang, B. Nosarzewski, T. P. Devereaux, G. Zhang, and M. C. Asensio, “Emergence of interfacial polarons from electron-phonon coupling in graphene/h-BN van der Waals heterostructures,” Nano Letters 18, 1082–1087 (2018).

[17] M.-L. Lin, Y. Zhou, J.-B. Wu, X. Cong, X.-L. Liu, J. Zhang, H. Li, W. Yao, and P.-H. Tan, “Cross-dimensional electron-phonon coupling in van der Waals heterostructures,” Nature Communications 10, 2419 (2019).

[18] D. Zhong, K. L. Seyler, X. Linpeng, R. Cheng, N. Sivadas, B. Huang, E. Schmidgall, T. Taniguchi, K. Watanabe, and M. A. McGuire, “Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics,” Science Advances 3, e1603113 (2017).

[19] S. Jiang, L. Li, Z. Wang, K. F. Mak, and J. Shan, “Controlling magnetism in 2D CrI$_3$ by electrostatic doping,” Nature Nanotechnology 13, 549–553 (2018).

[20] S. Jiang, J. Shan, and K. F. Mak, “Electric-field switching of two-dimensional van der Waals magnets,” Nature Materials 17, 406–410 (2018).

[21] B. Huang, G. Clark, D. R. Klein, D. MacNeill, E. Navarro-Moratalla, K. L. Seyler, N. Wilson, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, P. Jarillo-Herrero, and X. Xu, “Electrical control of 2D magnetism in bilayer CrI$_3$,” Nature Nanotechnology 13, 544–548 (2018).

[22] H. H. Kim, B. Yang, T. Patel, F. Sfigakis, C. Li, S. Tian, H. Lei, and A. W. Tsen, “One million percent tunnel magnetoresistance in a magnetic van der Waals heterostructure,” Nano Letters 18, 4885–4890 (2018).

[23] Z. Wang, I. Gutiérrez-Lezama, N. Ubrig, M. Kroner, M. Gibertini, T. Taniguchi, K. Watanabe, A. Imamoğlu, E. Giannini, and A. F. Morpurgo, “Very large tunneling magnetoresistance in layered magnetic semiconductor CrI$_3$,” Nature Communications 9, 2516 (2018).

[24] T. Song, X. Cai, M. W.-Y. Tu, X. Zhang, B. Huang, N. P. Wilson, K. L. Seyler, L. Zhu, T. Taniguchi, K. Watanabe, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, and X. Xu, “Giant tunneling magnetoresistance in spin-filter van der Waals heterostructures,” Science 360, 1214–1218 (2018).

[25] D. R. Klein, D. MacNeill, J. L. Lado, D. Soriano, E. Navarro-Moratalla, K. Watanabe, T. Taniguchi,
S. Manni, P. Canfield, J. Fernández-Rossier, and P. Jarillo-Herrero, “Probing magnetism in 2D van der Waals crystalline insulators via electron tunneling,” *Science* **360**, 1218–1222 (2018).

[26] H. H. Kim, B. Yang, S. Li, S. Jiang, C. Jin, Z. Tao, G. Nichols, F. Sfigakis, S. Zhong, C. Li, S. Tian, D. G. Cory, G.-X. Miao, J. Shan, K. F. Mak, H. Lei, K. Sun, L. Zhao, and A. W. Tsen, “Evolution of interlayer and intralayer magnetism in three atomically thin chromium trihalides,” *Proceedings of the National Academy of Sciences* **116**, 11131 (2019).

[27] H. H. Kim, B. Yang, S. Tian, C. Li, G.-X. Miao, H. Lei, and A. W. Tsen, “Tailored tunnel magnetoresistance response in three ultrathin chromium trihalides,” *Nano Letters* **19**, 5739–5745 (2019).

[28] M. Wu, Z. Li, T. Cao, and S. G. Louie, “Physical origin of giant excitonic and magneto-optical responses in two-dimensional ferromagnetic insulators,” *Nature Communications* **10**, 2371 (2019).

[29] S. Moser, L. Moreschini, J. Jacimović, O. Barisić, H. Berger, A. Magrez, Y. Chang, K. Kim, A. Bostwick, and E. Rotenberg, “Tunable polaronic conduction in anatase TiO$_2$,” *Physical Review Letters* **110**, 196403 (2013).

[30] J. J. Lee, F. T. Schmitt, R. G. Moore, S. Johnston, Y. T. Cui, W. Li, M. Yi, Z. K. Liu, M. Hashimoto, Y. Zhang, D. H. Lu, T. P. Devereaux, D. H. Lee, and Z. X. Shen, “Interfacial mode coupling as the origin of the enhancement of $T_c$ in FeSe films on SrTiO$_3$,” *Nature* **515**, 245–248 (2014).

[31] C. Chen, J. Avila, E. Frantzeskakis, A. Levy, and M. C. Asensio, “Observation of a two-dimensional liquid of Fröhlich polarons at the bare SrTiO$_3$ surface,” *Nature Communications* **6**, 8585 (2015).

[32] C. Cancellieri, A. S. Mishchenko, U. Aschauer, A. Filippetti, C. Faber, O. Barisić, V. Rogalev, T. Schmitt, N. Nagaosa, and V. N. Strocov, “Polaronic metal state at the LaAlO$_3$/SrTiO$_3$ interface,” *Nature Communications* **7**, 10386 (2016).

[33] Z. Wang, S. McKeown Walker, A. Tamai, Y. Wang, Z. Ristic, F. Y. Bruno, A. de la Torre, S. Riccó, N. C. Plumb, M. Shi, P. Hlawenka, J. Sánchez-Barriga, A. Varykhalov, T. K. Kim, M. Hoesch, P. D. C. King, W. Meevasana, U. Diebold, J. Mesot, B. Moritz, T. P. Devereaux, M. Radovic, and F. Baumberger, “Tailoring the nature and strength of electron-phonon interactions in the SrTiO$_3$ (001) 2D electron liquid,” *Nature Materials* **15**, 835–839 (2016).

[34] C. Verdi, F. Caruso, and F. Giustino, “Origin of the crossover from polarons to Fermi liquids in transition metal oxides,” *Nature Communications* **8**, 15769 (2017).

[35] K. Cho and Y. Toyozawa, “Exciton-phonon interaction and optical spectra – Self-trapping, zero-phonon line and phonon sidebands,” *Journal of the Physical Society of Japan* **30**, 1555–1574 (1971).

[36] D. Shcherbakov, P. Stepanov, D. Weber, Y. Wang, J. Hu, Y. Zhu, K. Watanabe, T. Taniguchi, Z. Mao,
[37] W. Jin, H. H. Kim, Z. Ye, S. Li, P. Rezaie, F. Diaz, S. Siddiq, E. Wauer, B. Yang, C. Li, S. Tian, K. Sun, H. Lei, A. W. Tsen, L. Zhao, and R. He, “Raman fingerprint of two terahertz spin wave branches in a two-dimensional honeycomb Ising ferromagnet,” Journal of Physics and Chemistry of Solids 1531–1549 (2016).

[38] J. F. Dillon, H. Kamimura, and J. P. Remeika, “Magneto-optical properties of ferromagnetic chromium trihalides,” Journal of the American Chemical Society 27, 1531–1549 (1966).

[39] I. Pollini, “Electron correlations and hybridization in chromium compounds,” Solid State Communications 106, 549–554 (1998).

[40] I. Pollini and G. Spinolo, “Intrinsic optical properties of CrCl3,” Physical Review B 98, 085406 (2018).

[41] D. T. Larson and E. Kaxiras, “Raman spectrum of CrI3: An ab initio study,” Physical Review B 98, 085406 (2018).

[42] S. Djurdjić-Mijin, A. Šolajić, J. Pešić, M. Šćepanović, Y. Liu, A. Baum, C. Petrovic, N. Lazarević, and Z. Popović, “Lattice dynamics and phase transition in CrI3 single crystals,” Physical Review B 98, 104307 (2018).

[43] J. Vitins and P. Wachter, “Eu and Yb chalcogenides: Model substances for multiphonon inelastic light scattering,” Journal of Magnetism and Magnetic Materials 3, 161–163 (1976).

[44] R. Merlin, G. Güntherodt, R. Humphreys, M. Cardona, R. Suryanarayanan, and F. Holtzberg, “Multiphonon processes in YbS,” Physical Review B 17, 4951 (1978).

[45] G. Güntherodt, R. Merlin, and P. Grünberg, “Spin-disorder-induced Raman scattering from phonons in europium chalcogenides. I. Experiment,” Physical Review B 20, 2834–2849 (1979).

[46] R. Zeyher and W. Kress, “Spin-disorder-induced raman scattering from phonons in europium chalcogenides. II. Theory,” Physical Review B 20, 2850–2863 (1979).

[47] R. C. C. Leite, J. F. Scott, and T. C. Damen, “Multiple-phonon resonant Raman scattering in CdS,” Physical Review Letters 22, 780–782 (1969).

[48] M. V. Klein and S. P. S. Porto, “Multiple-phonon-resonance raman effect in CdS,” Physical Review Letters 22, 782–784 (1969).

[49] R. M. Martin and C. M. Varma, “Cascade theory of inelastic scattering of light,” Physical Review Letters 26, 1241–1244 (1971).

[50] G. B. Osterhoudt, R. Carelli, K. S. Burch, F. Katmis, N. Gedik, and J. S. Moodera, “Charge transfer
in EuS/Bi$_2$Se$_3$ heterostructures as indicated by the absence of Raman scattering,” Physical Review B 98, 014308 (2018)

[51] T. Feldtmann, M. Kira, and S. W. Koch, “Phonon sidebands in semiconductor luminescence,” physica status solidi (b) 246, 332–336 (2009).

[52] H. Hübener, U. De Giovannini, and A. Rubio, “Phonon driven Floquet matter,” Nano Letters 18, 1535–1542 (2018).

[53] J. L. Lado and J. Fernández-Rossier, “On the origin of magnetic anisotropy in two dimensional CrI$_3$,” 2D Materials 4, 035002 (2017).

[54] P. Y. Yu, “Study of excitons and exciton-phonon interactions by resonant Raman and Brillouin spectroscopies,” in Excitons, edited by K. Cho (Springer Berlin Heidelberg, Berlin, Heidelberg, 1979) pp. 211–253.

[55] H. Fröhlich, “Electrons in lattice fields,” Advances in Physics 3, 325–361 (1954).

[56] L. Webster, L. Liang, and J.-A. Yan, “Distinct spin-lattice and spin-phonon interactions in monolayer magnetic CrI$_3$,” Physical Chemistry Chemical Physics 20, 23546–23555 (2018).

[57] G. D. Mahan, Many-particle physics (Springer Science & Business Media, 2013).

[58] D. C. Langreth, “Singularities in the X-ray spectra of metals,” Physical Review B 1, 471 (1970).

[59] M. de Jong, L. Seijo, A. Meijerink, and F. T. Rabouw, “Resolving the ambiguity in the relation between Stokes shift and Huang-Rhys parameter,” Physical Chemistry Chemical Physics 17, 16959–16969 (2015).

[60] F. M. Peeters and J. T. Devreese, “Scaling relations between the two- and three-dimensional polarons for static and dynamical properties,” Physical Review B 36, 4442–4445 (1987).

[61] Z. Sun, Y. Yi, T. Song, G. Clark, B. Huang, Y. Shan, S. Wu, D. Huang, C. Gao, Z. Chen, M. McGuire, T. Cao, D. Xiao, W.-T. Liu, W. Yao, X. Xu, and S. Wu, “Giant nonreciprocal second-harmonic generation from antiferromagnetic bilayer CrI$_3$,” Nature 572, 497–501 (2019).

[62] Y. Zhang, T. Holder, H. Ishizuka, F. de Juan, N. Nagaosa, C. Felser, and B. Yan, “Switchable magnetic bulk photovoltaic effect in the two-dimensional magnet CrI$_3$,” Nature Communications 10, 3783 (2019)
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Author contributions
W. J., R. H., and L. Z. conceived this project; S. T., Y. F., and H. L. synthesized and characterized the bulk CrI$_3$ single crystals; H. H. K., B. Y., F. Y., and A. W. T. fabricated and characterized the few-layer samples; Z. Y., G. Y., L. R. and R. H. performed the Raman measurements; J. H., W. J., and H. D. performed the linear absorption and photoluminescence spectroscopy measurements; W. J., X. L., R. H., and L. Z. analyzed the data with discussions with K. S.; W. J., X. L., R. H., and L. Z. wrote the paper and all authors participated in the discussions of the results.

Data availability
The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests
The authors declare no competing interests.
Fig. 1. **Exciton transitions in bilayer CrI$_3$.** PL (left, blue) and absorption (right, orange) spectra of a bilayer CrI$_3$ encapsulated between two hBN flakes and placed on the sapphire substrate, at 10, 40, and 80 K. A, B, and C denote three main exciton transitions at 1.51, 2.00, and 2.68 eV, and the orange arrow mark a shoulder mode at 1.79 eV appearing only at low temperature. Spectra at 10 K and 40 K are offset vertically for clarity. Inset shows the fitted full width at half maximum (FWHM) of PL spectra as a function of temperature, $\Gamma(T) = \Gamma_0 + \frac{\gamma}{\exp\left(\frac{\hbar \omega_{LO}}{k_B T}\right) - 1}$, (diamond symbols) and its fitting to the functional form with the first and second terms for homogeneous and e-ph coupling-induced broadening, respectively. Error bars indicate one standard error in fitting the FWHM of PL spectra.
Fig. 2. Polaronic character of exciton dynamics in bilayer CrI₃. a. Raman spectrum of bilayer CrI₃ acquired in the linearly crossed polarization channel at 70 K using a 633 nm laser. Inset shows the phonon Raman modes in both linearly parallel (red) and crossed (black) polarization channels, with the phonon modes labeled as A₁₋₃ and E₁₋₄, of A₉ and E₈ symmetries of the C₃i point group, respectively. The black arrow indicates the LO phonon frequency of importance, ωLO. The spectral intensities on the right side of the dashed line in the frequency range above 121 cm⁻¹ are scaled by a factor of 0.25. b. Zoom-in of the orange shaded area in the spectrum in a. Lorentzian profiles are fits to the periodic pattern indexed from N = 1 to N = 6. c. Plot of the fitted central frequency (ωₙ) of the Nth Lorentzian profile as a function of N. Solid line is a linear fit (ωₙ = NωLO) to the plot that yields a slope of ωₙ = 120.6 ± 0.9 cm⁻¹. d. Plot of the fitted linewidth Γₙ of the Nth Lorentzian profile as a function of N. Error bars are defined as one standard error of the fitting parameters.
Fig. 3. Enhanced e-ph coupling across the magnetic onset $T_C$ in bilayer CrI$_3$. a – b. Raman spectra of bilayer CrI$_3$ acquired at 40 K and 10 K, respectively. Lorentzian profiles are fit to the periodic patterns in the polaron Raman spectra. c. Plots of the fitted Lorentzian peak intensity ($A_N$) profiles at 70 K, 40 K, and 10 K. Solid curves are fits of the peak intensity profiles to the Poisson distribution functions. The data at 70 K and 40 K are vertically offset for clarity. d. Plot of 2D e-ph coupling constant ($\alpha_{2D}$) as a function of temperature. The dashed vertical line marks the magnetic onset $T_C = 45$ K, and the solid line is the fit to the functional form $\alpha_{2D}(T) = \begin{cases} 
A\sqrt{T_C-T} + B; & T \leq T_C \\ B; & T > T_C \end{cases}$. Error bars are defined as one standard error of the fitting parameters.
Fig. 4. Exciton-polaron dynamics across the magnetic phase transition from the layered AFM to FM in bilayer CrI₃. **a.** Raman spectra of bilayer CrI₃ acquired at 10 K in the circularly parallel polarization channels (RR and LL) with an applied out-of-plane magnetic field ($B_\perp$) of 1 T (top), 0 T (middle), and -1 T (bottom), respectively. RR(LL) is for selecting right-hand circularly polarized incident and scattered light. **b.** Plots of the fitted Lorentzian peak intensity profiles at all magnetic fields, showing a clear separation between the ones at 0 – 0.7 T (filled symbols, darker orange shade) and the rest at 0.8 – 1.4 T (open symbols, lighter orange shade). **c.** Plots of $\alpha_{2D}$ (left-axis) and $A_0$ (right-axis) as a function of the applied $B_\perp$. Solid lines are linear (gray) and step (orange) function fits to the magnetic field dependence of $\alpha_{2D}$ (gray square) and $A_0$ (orange circle), respectively. Error bars are defined as one standard error of the fitting parameters.
Supplementary Information

Evidence of the polaronic character of excitons in a two-dimensional semiconducting magnet CrI$_3$

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**S1. Second-order phonon modes in bilayer CrI$_3$**

Fig. S1 shows the comparison between Raman spectra in the frequency range of 90 – 140 cm$^{-1}$ (upper panel) and 180 – 280 cm$^{-1}$ (lower panel). The first-order phonon modes in the upper panel are labeled following the assignment shown in Fig. 2 of the main text. In the lower panel, a series of modes with weaker cross-section and broader linewidth are attributed to second-order phonon modes except the sharp one at 239 cm$^{-1}$. Based on the phonon band structure calculations in the literature (Phys. Rev. B 98, 104307 (2018) and Phys. Chem. Chem. Phys. 20, 23546-23555 (2018)), this 239 cm$^{-1}$ mode coincides with a computed $E_g$ mode, and therefore is labeled as $E_5$ here.

![Fig. S1. Raman spectra of bilayer CrI$_3$ in the range of 90 – 140 cm$^{-1}$ (upper) and 180 – 280 cm$^{-1}$ (lower) acquired in parallel (red) and crossed (blue) linear polarization channels at 70 K using a 633 nm laser. The spectra on the right side of the dashed line (top panel) are scaled by a factor of 0.25. The first-order phonon modes are labeled as $E_1$-$E_4$ and $A_3$ in upper panel and $E_5$ in the lower panel.](image)

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S2. Exciton-polaron in 2D CrI$_3$ with varying thickness

We have performed both temperature and magnetic field dependence measurements on three layer (3L), four layer (4L), and five layer (5L) CrI$_3$ flakes.

1) Temperature dependence in 3L, 4L, and 5L CrI$_3$

Fig. S2. Temperature dependent Raman spectra taken on a. 3L, b. 4L, and c. 5L CrI$_3$ with the same analysis as Fig. 3 in the main text.
Fig. S2 shows temperature dependent Raman spectroscopy results for 3L, 4L, and 5L CrI₃. We have performed the same analysis as we did for bilayer (2L) CrI₃ to extract the peak intensity ($A_N$) v.s. $N^{th}$ order for the periodic broad modes for the temperature range 10 – 65 K (with one spectrum every 5 K for all three thicknesses). We fitted $A_N$ with the Poisson distribution function to extract the electron-phonon coupling strength $\alpha_{2D}$ for each temperature. We finally plotted $\alpha_{2D}$ as a function of temperature. On a qualitative level, the temperature dependence results for these three thicknesses are consistent with that for 2L CrI₃ in the main text Fig. 3.

**Fig. S3.** a. Magnetic field dependent Raman spectra taken on 3L, 4L, and 5L CrI₃ in the RR polarization channel with the same analysis as Fig. 4 in the main text. b. Magnetic field dependence of the fitted $A_0$, the overall intensity of the Poisson profile for the polaron spectra. c. Magnetic field dependence of the fitted e-ph coupling strength.

2) **Magnetic field dependence in 3L, 4L, and 5L CrI₃**

Fig. S3 shows the magnetic field dependence for CrI₃ flake with three different thicknesses, 3L, 4L, and 5L. We have done the same analysis as that for 2L CrI₃ to extract the overall polaron intensity and e-ph coupling constant for the polaron spectra at varying magnetic fields, with the results showing in Fig. S3b and S3c. The polaron intensity shows a step-function like decrease in RR channel at a critical magnetic field $B_C = \sim 1.7$ T for all three thicknesses, which is consistent with the layered AFM to FM transition in 3 – 5L CrI₃, while the e-ph coupling constant remains
nearly constant across $B_C$. Despite the difference in $B_C$ between 2L and 3 – 5L CrI$_3$, their magnetic field dependence are qualitatively the same.

3) **Layer number dependence of the electron-phonon coupling in CrI$_3$**

Fig. S4 summarizes the layer number dependence of the e-ph coupling constant in CrI$_3$.

**Fig. S4.**  
**a.** Temperature dependence of the e-ph coupling constant for 2 – 5 L CrI$_3$. Thick orange curve is the guide to the eye that mimics the order parameter temperature dependence.  
**b.** The e-ph coupling constant as a function of layer number.
S3. Anti-Stokes polaron Raman spectra in bilayer CrI₃

As shown in Fig. S5a, there is very limited signal on the anti-Stokes side. Only one phonon mode at -107 cm⁻¹ is observed at 55 K but not at 10 K. The peak intensity profile for the periodic broad modes remain consistent with what we found in the main text Fig. 2 and 3, even with the consideration of the 0th order mode. We did further analysis to the only anti-Stokes phonon mode, plotted ln(Iₘ/Iₘ₋ₑ) as a function of 1/T in Fig. S5b, and found that it fits well with the desired functional form of \( Iₘ₋ₑ(\omega) = Iₘ(\omega)\left(\frac{\omega + \omega_0}{\omega - \omega_0}\right)^2e^{-\hbar\omega/k_BT} \), where \( Iₘ(\omega) \) and \( Iₘ₋ₑ(\omega) \) are intensities of the Stokes and anti-Stokes phonon modes at frequency \( \omega = 107 \text{ cm}^{-1} \), \( \omega_0 \) is the excitation laser frequency, and \( T \) is the temperature. This result indicates that there is no detectable thermal heating effect from our excitation laser, which is consistent with the onset temperature of 45 K in the plot of electron-phonon coupling constant v.s. temperature in main text Fig. 3d.

Fig. S5. a. Raman spectra extending to anti-Stokes side taken on a bilayer CrI₃ at \( T = 12 \text{ K} < T_C \) (top panel) and \( T = 55 \text{ K} > T_C \) (bottom panel) in linearly crossed polarization channel. The orange arrow labels the only observable anti-Stokes phonon mode at -107 cm⁻¹. b. Plots of ln(Iₘ/Iₘ₋ₑ) v.s. 1/T for the phonon mode at 107 cm⁻¹, with the formula above showing the relation between \( Iₘ(\omega) \) and \( Iₘ₋ₑ(\omega) \), intensity of Stokes and anti-Stokes phonon mode at frequency \( \omega \).
S4. Discussions on differences between the polaron and multiphonon process Raman

Below, we explain the difference between the periodic broad modes and phonon overtones.

1) Difference in Raman lineshape:
The Raman spectrum for the multiphonon process shows sharp peaks at integer numbers of the LO phonon frequency with significantly greater linewidth at higher order processes (e.g., PRL 22, 780 (1969) and more others). In the Raman spectrum for CrI₃, there are also contributions from the multiphonon process, corresponding to the sharp phonon modes (linewidth in order of 1 cm⁻¹) that survive up to the 3rd order at T = 10 K (1st, 2nd, and 3rd order phonon modes are labeled in Fig. S6). In addition and in contrast, (1) the Raman spectrum for CrI₃ features periodic broad modes (linewidth of ~70 cm⁻¹) centered at integer numbers of 120 cm⁻¹ without a steep increasing in the linewidth at higher orders. (2) this broad mode survives up to the 8th order, much higher than the 3rd order for the multiple phonon process in CrI₃.

For the EuX case, it is worth noting that the LO phonon mode linewidth is broad at room temperature (PRB, 20, 2834 (1979)). This is because of (i) the scattering process involving one phonon and one spin; and (ii) the material systems having spin-disorder effect. But the linewidth increases significantly at higher order process, which is in contrast to that of the periodic broad modes in CrI₃.

Fig. S6. A representative Raman spectrum of bilayer CrI₃ at 10 K over a wide frequency range showing both the multiphonon modes up to the 3rd order (labeled in blue) and the periodic broad modes up to the 8th order (labeled in orange).
2) Difference in the microscopic origin:
The multiphonon process originates from the cascade process of electron (hole) scattered by phonons before the electron-hole recombination. In contrast, the periodic broad modes in CrI$_3$ are from the scattering of electron (hole) between the phonon-dressed electronic states. The linewidth (the inverse of the lifetime) for the broad modes in CrI$_3$ is dominated by the linewidth of these electronic states which are supposed to be much broad than that of phonons. Such phonon-dressed electronic bands have been reported in a few systems (e.g., SrTiO$_3$, 1 unit cell FeSe/SrTiO$_3$, etc) using the ARPES technique.

For the case of EuX, because of the antisymmetric nature of the phonon mode of relevance, the scattering process for the first order include one LO phonon and one spin, and so on so forth for the higher order phonon modes.

3) Difference in the intensity profile as a function of $N^{th}$ order:
Because of the cascade process, the multiphonon process often shows the exponential decay of the scattering intensity with respect to the $N^{th}$ order of the phonon process. In contrast, the broad modes in CrI$_3$ Raman spectrum obeys the Poisson distribution of the scattering intensity with respect to the $N^{th}$ mode order, which is consistent with the spectral weight profile for the phonon-dressed electronic states.

For the EuX case, the constant decay for the multiphonon mode intensity with increasing $N^{th}$ order is consistent with the cascade multiple phonon process, and therefore support its distinction from the periodic broad modes of our interest in the current manuscript.

4) Difference in the presence of the relevant LO phonon in Raman:
The last but not the least point to show: In the multiphonon process, the relevant LO phonon shows up in the Raman spectra as the sharpest 1$^{st}$ order phonon mode. In contrast, the relevant LO phonon at $\sim$120 cm$^{-1}$ in this manuscript is Raman inactive and therefore not present in the 1$^{st}$ order phonon spectra (see Fig. S7).

For the EuX case, the first order LO phonon is present in the Raman spectra, in contrast to the
absence of the LO phonon mode at 120.6 cm$^{-1}$ here.

Given the listed differences between the multiphonon and periodic broad modes, we believe what we observed here in CrI$_3$, the periodic broad feature that survives up to the 8th order at 10 K, is distinct from the multiphonon modes which are also present in CrI$_3$ but only up to the 3rd order at 10 K.

![Graph](image)

**Fig. S7.** Two representative 1st order phonon Raman spectra (in the linearly parallel and crossed polarization channels) at $T = 70$ K showing all Raman active phonon modes in the frequency range of 70 – 150 cm$^{-1}$. The vertical arrow indicates 120.6 cm$^{-1}$, the frequency for the LO phonon responsible for the periodic broad modes. It is clear that this LO phonon mode is not detectable in the 1st order phonon Raman spectra.
S5. Periodic pattern in Raman spectrum observed in bulk CrI$_3$

We performed Raman spectroscopy measurements on a freshly cleaved CrI$_3$ bulk crystal using identical experimental conditions as that taken on bilayer CrI$_3$ samples. Fig. S8 shows a Raman spectrum acquired at 70 K. A similar periodic pattern as that in bilayer CrI$_3$ is observed in bulk CrI$_3$ and is fitted by a summation of Lorentzian profiles of the form $\sum N \frac{A_N (\Gamma_N/2)^2}{(\omega - \omega_N)^2 + (\Gamma_N/2)^2}$. Inset shows the plot of the fitted central frequency $\omega_N$ as a function of $N$, whose linear fit provides the periodicity of 121.3 ± 1.2 cm$^{-1}$. This periodicity, i.e., the frequency of the participating polar LO phonons in the formation of exciton-polarons, is slightly greater than that of 120.6 ± 0.9 cm$^{-1}$ in bilayer CrI$_3$. This can be attributed to the additional interlayer coupling on both sides of a layer in bulk CrI$_3$, which is supported by similar amount of blue shift for the Raman active phonon modes. The consistency between bulk and bilayer CrI$_3$ definitively rules out the possibility of the polaron in bilayer CrI$_3$ resulting from the interfacial coupling with the hBN capsulation layers or the SiO$_2$/Si substrate.

Fig. S8. Raman spectrum of bulk CrI$_3$ acquired in the crossed linear polarization channel at 70 K using a 633 nm laser. Lorentzian profiles (orange shade) are fits to the multiples. Inset shows the plot of the central frequencies ($\omega_N$) as a function of the index $N$. The frequency of the LO phonon ($\omega_{LO}$) is extracted by a linear fit to $\omega_N$ (solid line).
S6. Polaron Raman spectra of bilayer CrI$_3$ in four circular polarization channels

Above $B_C$, (i) the ferromagnetic order has a net magnetization, and therefore the system responds differently to LL and RR (the two polarization geometries are related by the time-reversal operation); (ii) the ferromagnetic order has the inversion symmetry, and therefore Raman can only detect parity even modes.

Below $B_C$, (i) the layered antiferromagnetic order has no net magnetization, and therefore the system responds equivalently to LL and RR (the two polarization geometries are related by the time-reversal operation); (ii) the layered antiferromagnetic order breaks inversion symmetry, and therefore it releases the constraint of only parity even modes being Raman active.

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Fig. S9. Raman spectra taken in all four circular polarization channels at 0 T (left), 1 T (middle), and -1 T (right).
Fig. S10. Raman spectra taken on a bilayer CrI$_3$ with three different incidence wavelengths: 473 nm, 532 nm, and 785 nm, in the linearly polarized parallel channel at 12 K. Black arrows in the 532 nm spectrum indicates the phonon modes of bilayer CrI$_3$. 

Fig. R21. Linearly parallel.