

Light induced electron spin resonance properties of van der Waals CrX_3 ($\text{X} = \text{Cl}, \text{I}$) crystals

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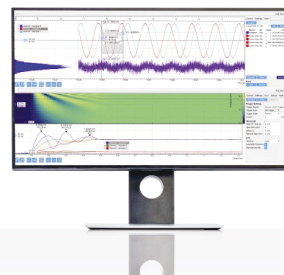
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ABSTRACT

The research on layered van der Waals (vdW) magnets is rapidly progressing owing to exciting fundamental science and potential applications. In bulk crystal form, CrCl_3 is a vdW antiferromagnet with in-plane ferromagnetic ordering below 17 K, and CrI_3 is a vdW ferromagnet below 61 K. Here, we report on the electron spin resonance (ESR) properties of CrCl_3 and CrI_3 single crystals upon photo-excitation in the visible range. We noticed remarkable changes in the ESR spectra upon illumination. In the case of CrCl_3 , at 10 K, the ESR signal is shifted from $g = 1.492$ (dark) to 1.661 (light), the linewidth increased from 376 to 506 Oe, and the signal intensity is reduced by 1.5 times. Most interestingly, the observed change in the signal intensity is reversible when the light is cycled on/off. We observed almost no change in the ESR spectral parameters in the paramagnetic phase (> 20 K) upon illumination. Upon photo-excitation of CrI_3 , the ESR signal intensity is reduced by 1.9 times; the g -value increased from 1.956 to 1.990; the linewidth increased from 1170 to 1260 Oe at 60 K. These findings are discussed by taking into account the skin depth, the slow relaxation mechanism, and the appearance of low-symmetry fields at the photo-generated Cr^{2+} Jahn–Teller centers. Such an increase in the g -value as a result of photo-generated Cr^{2+} ions is further supported by our many-body wavefunction calculations. This work has the potential to extend to monolayer vdWs magnets by combining ESR spectroscopy with optical excitation and detection.

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van der Waals (vdW) layered magnets, such as CrX_3 ($\text{X} = \text{Cl}, \text{I}$) with a unique atomic-level exfoliable structure and rich physical properties (e.g., ferromagnetism at the atomic limit), are promising materials for next generation spintronic and magneto-electronic applications.^{1–5} Their outstanding features such as the interplay of dimensionality, correlation, charge, orbital character, and topology of being susceptible to a large variety of external stimuli make the versatile control of 2D magnetism possible by electrical, chemical, and optical approaches.⁴ The electric field, electrostatic doping, and mixed halide chemistry have been shown to control the magnetic properties (magnetization, coercive field, and magnetic order) of these materials.^{2,3,6} Unlike the above approaches, light is a particularly intriguing tool, which could potentially enable remote and rapid control of magnetic properties of layered vdW magnets that are susceptible to external stimuli, with much less energy consumption to develop spin electronics.

To advance the frontier of knowledge, photo-excitation investigations need to be extended to the above vdW materials. Numerous theoretical works^{7–10} predicted that there is a strong coupling between light and magnetism and strong magneto-optical effects⁷ in vdW magnets due to complete spin polarization in conduction and valence bands. Previous researchers have measured the magnetic properties of these layered materials using light.^{1–5} However, controlling their magnetic properties using light has remained largely unexplored. Since the magnetic properties of bulk crystals serve as a basis for the understanding of the magnetic phenomenon in reduced dimensions, e.g., in few or monolayer CrX_3 , a profound knowledge and understanding is evidently needed, especially considering that magnetic mono- and bilayers of CrX_3 have now become accessible.

In CrX_3 , Cr^{3+} ions are arranged in a honeycomb network and located at the centers of edge sharing octahedral of six halogen atoms.

CrI_3 is a ferromagnet¹¹ with a Curie temperature (T_C) = 61 K, and CrCl_3 is an in-plane ferromagnet¹² and out-of-plane antiferromagnet (AFM) with an ordering temperature (Néel temperature, T_N) near 17 K. To note, with the application of a few hundred Oersted magnetic field, CrCl_3 can be turned into a ferromagnet.¹³ Therefore, most likely, CrCl_3 turns to a complete ferromagnet during the X-band electron spin resonance (ESR) measurements (not before the magnetic field was swept) as several thousand Oersted magnetic fields are applied to detect the Electron spin resonance (ESR) signal. In essence, during the ESR measurements, the ground states of these two compounds can be approximated as ferromagnetic state.

ESR spectroscopy is an indispensable technique for studying magnetic interactions in materials such as CrX_3 containing unpaired electron spins. ESR spectroscopy has been extensively employed to study the spin interactions in other low dimensional materials such as graphene nanoribbons, carbon nanotubes, and other vdW crystals.^{14–20} There have been no prior reports appearing in the literature on the study of the photo-excited ESR properties of CrX_3 though they are known to be magnetically and optically active. In this Letter, by employing experimental and theoretical approaches, we report that the ESR properties—reflective of local magnetic exchange interactions in CrX_3 —can be tuned through optical means.

The experimental materials, methods, and procedures for quantum chemistry calculations are discussed in the [supplementary material](#). To trace the ferromagnetic ordering temperature (T_C), the temperature-dependent magnetic measurements were performed (under dark) on CrCl_3 single crystals and confirmed that the magnetic order appeared near 17 K as shown in [Fig. 1\(a\)](#), which is consistent with the literature.¹² Isothermal magnetization measurements [inset of [Fig. 1\(a\)](#)] show the expected soft ferromagnetic nature of this compound. The schematic structure of CrX_3 is shown in [Fig. 1](#) of the [supplementary material](#). As shown in the [supplementary material](#), [Figs. 2\(a\)](#) and [2\(d\)](#) present the X-band (9.45 GHz) ESR spectra (0–7 kOe) recorded on CrCl_3 at 10 K and 20 K when the light is ON (shown in red) and OFF (shown in black) in the ferromagnetic phase, respectively. Also included is the light on minus light off signal (shown in blue). In the [supplementary material](#), [Figs. 2\(b\)](#) and [2\(c\)](#) depict the ESR signal intensity as a function of time (in seconds) when the light is ON, OFF, and ON again. As it can be noted, at 10 K, the signal intensity at 3870 Oe drops to a much lower stationary value in less than half a second once the light is OFF and the signal is completely reversible to its original level once the light is ON again in few milliseconds, which is remarkably close to the (radiative luminescence) lifetime (13-ms) reported in the literature^{21,22} for Cr^{3+} . The stationary value reached during the photo-excitation was found to depend on the intensity of the light. This means that light is strongly coupled with the magnetic behavior of CrCl_3 .

The ESR spectral parameters such as the g-value, linewidth, and integrated intensity for both light ON and OFF signals, as plotted in [Figs. 1\(b\)–1\(d\)](#) as a function of temperature, were obtained from the computer-generated fits using a Dysonian line shape ([supplementary material](#) [Fig. 3](#)). As the data suggest, distinct ESR spectral parameters are noted upon photo-excitation in the ordered magnetic phase (<17 K) of CrCl_3 . The spectral parameters are the same in the paramagnetic phase (>17 K) of CrCl_3 . Several interesting features can be noted. First, the signal is strongly shifted from $g = 1.492$ (dark) to 1.661 (light). Second, the ESR signal is broadened from 376 Oe to

506 Oe. Third, the ESR signal intensity is reduced by 1.5 times. The obtained ESR spectral parameters (resonance field/g-value, linewidth) under dark are the benchmark signatures of Cr^{3+} ($S = 3/2$) ions in the octahedral site, consistent with the previous reports²³ on this compound and not related to any defect-related spin centers. ESR signal intensity is decreased by increasing the incident light intensity that can be attributed to the change in the skin depth.²⁴ The photo-magnetic effects appeared only below the ordering temperature of 17 K ([supplementary material](#) [Fig. 2](#)) and increased with a decrease in the temperature.

The ESR signal is also measured above 20 K in the paramagnetic phase, and the data are plotted in [supplementary material](#) [Figs. 2\(e\)–2\(g\)](#) at the temperatures of 50 K, 100 K, and 295 K, respectively. As it can be noted, the ESR signals before and after the light is ON almost overlap. It should be mentioned that the pure heating effect takes at least several seconds; however, the response in the present sample is much faster (<0.5 s). Heating mainly comes from IR light, but our LED emission does not contain an IR component. Weak signals appeared at the low field side of the spectrum collected at 10 K, which could be due to the small ferromagnetic inhomogeneity or isolated Cr^{3+} present²⁵ in the crystal and disappeared as the measurement temperature is increased.

Now, we will present our data on CrI_3 . To determine T_C , the magnetization (dark) was recorded as a function of temperature and magnetic field. As plotted in [Fig. 2\(a\)](#), CrI_3 shows a clear T_C at 60 K. Also, the magnetic hysteresis loop changes its curvature from ferromagnetic to paramagnetic across the magnetic phase transition at 60 K [inset of [Fig. 2\(a\)](#)], consistent with previous works.¹¹

Once we knew the T_C , the light-induced ESR measurements were performed on CrI_3 across the T_C (10 K, 30 K, 60 K, 65 K, and 100 K). Similar to the case of CrCl_3 , the light in the visible region is employed for excitation. First, we will begin discussing the data collected in the paramagnetic phase (>60 K). Quite strikingly, unlike in the case of CrCl_3 , we observed significant changes in the ESR spectral properties in the paramagnetic phase. The data are plotted in [supplementary material](#) [Figs. 4\(a\)–4\(e\)](#). The ESR signals were fitted with the Dysonian line shape equation²⁶ ([supplementary material](#) [Fig. 5](#)), and the ESR spectral parameters are plotted in [Figs. 2\(b\)–2\(d\)](#) as a function of temperature. The ESR signal is shifted from $g = 1.956$ to 1.990 [[Fig. 2\(b\)](#)], and the signal is broadened from the peak-to-peak linewidth of 1170–1260 Oe [[Fig. 2\(c\)](#)]. Most notably, upon photo-excitation, we noticed that there is a stronger quenching of ESR signal intensity by 1.9 times measured at 60 K [[Fig. 2\(d\)](#)]. As presented in the [supplementary material](#), [Figs. 3\(d\)](#) and [3\(e\)](#) show the time dependence of ESR signal intensity when the light is ON and OFF measured at 60 K and 100 K, respectively. The decrease in ESR signal intensity is directly proportional to the intensity of incident light. Most importantly, the ESR signal is reversible immediately upon switching OFF the light. This observation is consistently noticed even at other higher temperatures of 65 and 100 K in the paramagnetic phase. However, in the ferromagnetic phase (< 60 K), we found that ESR signals are irreproducible ([supplementary material](#) [Fig. 6](#)). Most likely, it could be due to the strong interaction of light with magnetic domains, which causes instability of ferromagnetic domains in CrI_3 .²⁷ The measurement was repeated even after cooling the sample under the magnetic field of 3000 Oe (to produce single ferromagnetic domain). However, we noticed that the results remain unaffected. Upon closer inspection, the

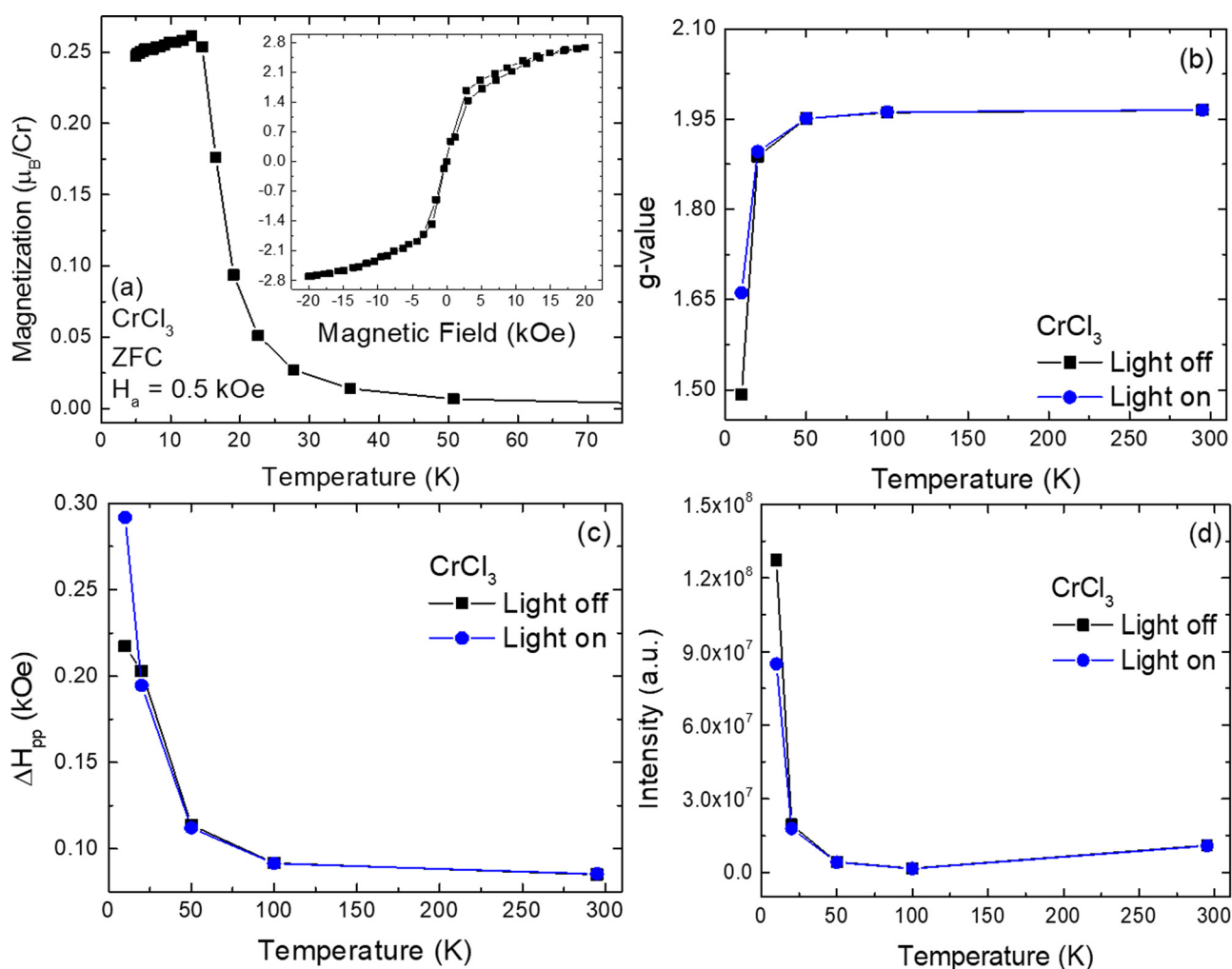


FIG. 1. (a) The Zero-Field-Cooled (ZFC) temperature dependence of the magnetization collected from CrCl₃ in the out-of-plane direction with an applied field (H_a) of 0.5 kOe. The magnetic order appeared at 17 K, consistent with Ref. 12. The inset shows the isothermal magnetization curve of CrCl₃ measured at 2 K. The temperature dependences of the g-value (b), the intensity (c), and the linewidth (d) of the ESR signal collected with light ON (in blue) and OFF (in black) from CrCl₃.

g-value and linewidth obtained from these two compounds are quite different and are attributed to magnetic anisotropy arising mostly from the spin-orbit coupling on I^- , which exceeds that on Cr^{3+} or Cl^- by more than an order of magnitude.^{11–13,28}

We have studied the magnetic properties of CrI₃ upon photo-excitation in ferromagnetic (50 K, 3 T—instrument limit) and paramagnetic regions (100 K) as plotted in Fig. 3. The data are plotted and compared with those of pristine (without light) CrI₃. The isothermal (50 K) magnetization of pristine CrI₃ is consistent (1.8 μ_B/Cr , slightly lower than 2 μ_B/Cr) with the previous work.¹¹ The results show that the magnetization (at 30 kOe) increased upon photo-excitation with ligand to metal charge transitions LMCT 1e (642 nm) and LMCT 2e (459 nm). It is most likely that the increase in magnetization (at 50 K) corresponds to the (in part) formation of Cr^{2+} ($S = 2$). The increase in the magnetization upon 642 nm photo-excitation is also reflected in the increase (3.9–4.9 μ_B/Cr) of effective magnetic moment (μ_{eff})

obtained through Curie–Weiss fits. Therefore, as discussed later in this manuscript, the magnetic behavior can be due to the combination of Cr^{3+} and Cr^{2+} and formation of two sub-magnetic systems.

Based on our experimental findings, we attempt to understand the effect of light on the ESR spectral properties of CrX₃. We will first consider the case of CrCl₃. As can be seen, almost no changes in the paramagnetic phase of this material upon illumination were observed, and hence, we will not discuss this further. Instead, we will focus our effort on its magnetically ordered phase.

Our experimental findings presented here resemble those of previous works,^{24,29,30} where the photo-magnetic effects were reported on chromium-based chalcogenide ferromagnetic semiconductor, namely, CdCr₂Se₄ associated with Cr^{3+} . The authors found that the ESR spectral properties such as ESR signal intensity, resonance field, and signal width are modified upon photo-excitation in the ferromagnetic phase (<130 K) of CdCr₂Se₄, and no changes were observed in the

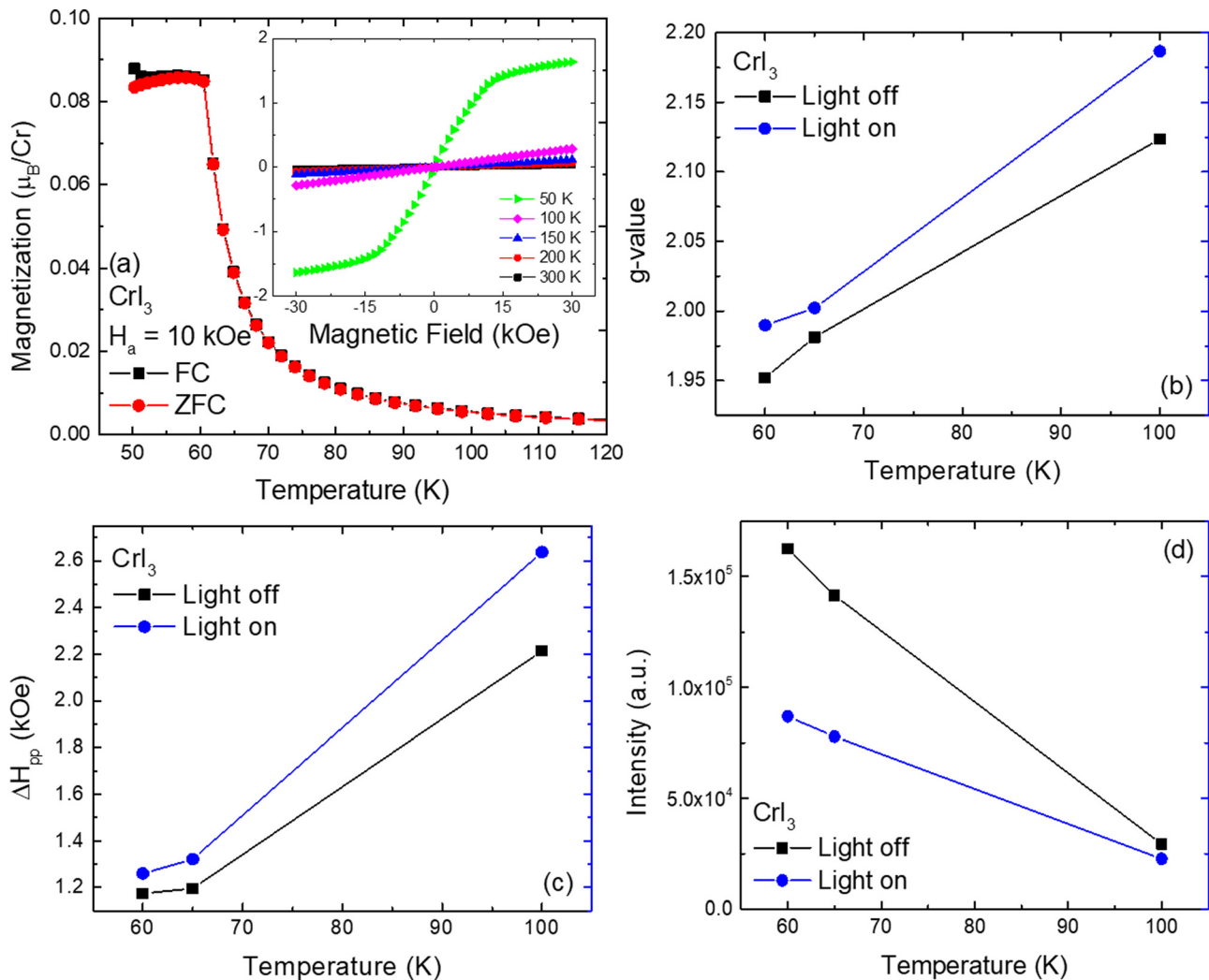


FIG. 2. (a) Variation of (in-plane) magnetization as a function of magnetic field (M-H) recorded at various temperatures on CrI₃. The inset shows the ZFC and Field-Cooled (FC) temperature-dependent magnetization curves collected with an applied field (H_a) of 10 kOe, consistent with Ref. 11. The temperature dependences of the g-value (b), the linewidth (d), and the intensity (c) of the ESR signal collected with light ON (in blue) and OFF (in black) from CrI₃.

paramagnetic phase (>130 K). This situation is exactly similar to the present case. This leads us to adopt the mechanisms here.

The photo-induced electronic transitions create Cr^{2+} ions in CrX_3 according to the scheme $\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$. The photo-activated electrons from the valence band are trapped on the octahedral Cr^{3+} sites, creating Cr^{2+} centers. They are assumed to be formed between the valence band and the Cr^{2+} energy level situated below the bottom of the conduction band.

The experimental results can be interpreted within the framework of a band model²⁴ (supplementary material Fig. 7). At a distance of 3.02 eV from the valence band, there is a narrow conduction band consisting of Cr^{2+} ($3d^4$) electrons. The transition between these two bands corresponds to a change in the chromium-ion valence according to the scheme $\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$. The observed light-induced changes in the ESR parameters may be caused by photo-induced

electron transitions between the valence band and localized Cr^{2+} ($d, 4 S = 2$) levels situated at a distance of 0.08 eV below the bottom of the conduction band. The observed light-induced decrease in ESR signal intensity may be caused by the photo-induced electron transitions between the above-mentioned Cr^{2+} levels and the broad conduction band from which the recombination process occurs much faster. It should be noted that the Cr^{2+} ESR signal could not be detected at an X-band frequency of 9.45 GHz at any measured temperatures, due to the shorter relaxation time and high zero field splitting.³¹

The changes in the g-value and signal width could be explained by taking into account the following two different mechanisms: (i) the slow relaxation mechanism in which the observed changes are attributed to Cr^{2+} and (ii) the appearance of random low-symmetry fields acting on the Jahn-Teller Cr^{2+} ions on the octahedral sites. In order to assess whether the observed increase in the g-value is related to the

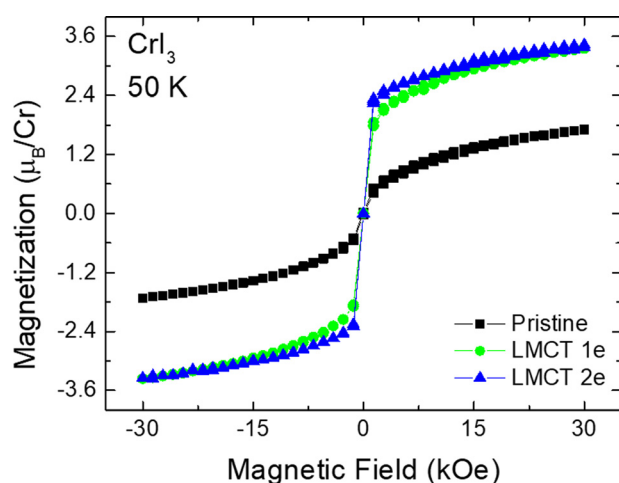


FIG. 3. Isothermal (50 K, 3 T) magnetization collected on CrI_3 upon photo-excitation with ligand to metal charge transition LMCT 1e (642 nm) and LMCT 2e (459 nm). For comparison, the data obtained from the dark state (pristine) are also included.

photo-generated Cr^{2+} ions, we performed quantum chemistry calculations on finite-size models derived from the experimental crystal structure.^{11,12} The models consist of a Cr-centered octahedral unit treated at the correlated level surrounded by the three nearest-neighbor octahedral units treated at the Hartree-Fock level. Such models are further embedded in an array of point charges fitted to the Madelung potential of the corresponding crystal lattice. As a first step, we have obtained multiconfiguration wavefunctions through complete-active-space self-consistent-field (CASSCF) computations.³² This was accomplished using an active space consisting of either three (for Cr^{2+} ions) or four (for Cr^{3+} ions) electrons residing in the three t_{2g} and two e_g orbitals at the central Cr site. CASSCF wavefunctions were optimized for the lowest quartet and five doublet states (one triplet, two quintet, and three singlet states) in the case of Cr^{3+} (Cr^{2+}) ions, which subsequently entered the spin-orbit treatment to yield spin-orbit coupled states. As a second step, single and double excitations from the Cr $3d$ and ligands' p valence shells are accounted for in the multireference configuration-interaction (MRCI) calculations.^{33,34} g -values were obtained by means of the methodology devised³⁵ for the ground state ($S = 3/2$) of both CrCl_3 and CrI_3 systems, in which the Cr ion features a formal $3+$ oxidation state. We remark that a similar computational strategy was successfully adopted in earlier quantum chemistry studies for a number of honeycomb lattice systems,^{36–39} including monolayer CrI_3 .³⁹

We found g -values of 1.42 for CrCl_3 and 1.92 for CrI_3 . In addition, we performed calculations assuming Cr^{2+} octahedral units, obtained by adding an extra electron at the Cr site and properly adapting the embedding to ensure charge neutrality. The g -values obtained in the case of Cr^{2+} ions are 1.79 for CrCl_3 and 2.08 for CrI_3 . This drastic change in the g -values is in line with the experimental findings discussed above, hence indicating that the reduction of Cr^{3+} – Cr^{2+} ions is at the origin of the observed photo-induced evolution of the ESR spectra. This is also supported by our recent ultrafast optical pump-probe measurements (not shown) on CrI_3 . We suggest that the slight discrepancy between the quantum chemistry and experimental data can

be traced back to the fact that only a fraction of Cr^{3+} ions are converted into the Cr^{2+} ions upon photo-excitation.

As learned from the above discussion, the system under investigation consists of two subsystems. The first is the ferromagnetically ordered Cr^{3+} ions, in which the spin-orbit coupling is known to be quenched. The second subsystem is formed by photo-generated Cr^{2+} . This ion is characterized by strong spin-orbit coupling (40 – 60 cm^{-1}). These two subsystems are coupled by an exchange interaction that, in general, is anisotropic. The interaction between these two subsystems can slow down the spin dynamics and cause the increase in the linewidth as well as the g -value due to the introduction of spin-orbit coupling from Jahn–Teller distorted Cr^{2+} ions.

Similar mechanisms can be extended to the case of photo-induced ESR spectral properties of CrI_3 , in which the light-induced changes are much stronger. In addition, the g -value and the linewidth of CrI_3 are much higher than those of CrCl_3 due to strong spin-orbit coupling of I as well as ligand-induced giant magnetic anisotropy.¹³ The photo-induced ESR spectral properties in the ferromagnetic phase of CrI_3 could not be reproduced. It can happen that the light-induced Cr^{2+} centers strongly interact with the ferromagnetic domains and modify the domain wall thickness and domain-wall mobility. That can cause the instability in the domain structure as was observed²⁷ in the case of FeBiO_3 . However, the question as to why the photo-induced ESR spectral properties are not observed in the paramagnetic phase of CrCl_3 remains to be answered.

To conclude, we reported remarkable changes in the ESR spectra of CrX_3 upon illumination. In the case of CrCl_3 , in the antiferromagnetic phase, with the light ON, it is observed that the ESR signal is strongly shifted from $g = 1.492$ (dark) to 1.661 (light), significantly broadening the signal from 376 (dark) to 506 Oe, and the signal intensity is strongly reduced by 1.5 times. Most importantly, the signal intensity is found to be completely reversible. In the case of CrI_3 , drastic changes were noted upon photo-excitation with the visible light. The ESR signal intensity is reduced by 1.9 times; the g -value increased from 1.956 to 1.990; the linewidth increased from 1170 to 1260 Oe in the paramagnetic phase. Most likely, the photo quenching effect, the slow relaxation mechanism, and the appearance of low-symmetry fields at the photo-generated Cr^{2+} Jahn–Teller centers, supported by theoretical calculations, could explain the changes in ESR spectral properties upon photo-excitation. This effort forms a significant step forward toward extending this type of work to mono- and bilayers of CrX_3 , which may provide unprecedented opportunities to study the light-induced magnetism in the two-dimensional limit.

See the [supplementary material](#) for the experimental methods and materials, magnetic properties, additional ESR measurements and analysis, and quantum chemical calculations performed on CrCl_3 and CrI_3 .

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Geosciences, and Biosciences, through the Argonne National Laboratory under Contract No. DE-AC02-06CH11357. R.Y. was supported by the Sinergia Network NanoSkyrmionics (Grant No. CRSII5-71003). M.P. was supported by the Swiss National Science Foundation (Grants Nos. 162612 and 172543). Calculations were performed at the Swiss National Supercomputing Centre (CSCS) under Project No. s832.

DATA AVAILABILITY

The data that support the findings of this study are available within this article and its [supplementary material](#).

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