

Spin-Forbidden Excitations in the Magneto-optical Spectra of CrI₃ Tuned by Covalency

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Spin-forbidden ($\Delta S \neq 0$) multiplet excitations and their coupling to magnetic properties are of increasing importance for magneto-optical studies of correlated materials. Nonetheless, the mechanisms for optically brightening these transitions and their generality remain poorly understood. Here, we report magnetic circular dichroism (MCD) spectroscopy on the van der Waals ferromagnet (FM) CrI₃. Previously unreported spin-forbidden ($\Delta S = 1$) $^4A_{2g} \rightarrow ^2E_g/{}^2T_{1g}$ Cr³⁺ *dd* excitations are observed near the ligand-to-metal charge-transfer excitation threshold. The assignment of these excitations and their Cr³⁺ multiplet character is established through complementary Cr *L*₃-edge resonant inelastic x-ray scattering measurements along with charge-transfer multiplet calculations and chemical trends in the chromium trihalide series (CrX₃, *X* = Cl, Br, I). We utilize the high sensitivity of MCD spectroscopy to study the thickness-dependent optical response. The spin-forbidden excitations remain robust down to the monolayer limit, and we observe a significant magnetic-field dependence of the MCD spectrum across the antiferromagnetic-to-FM transition in few-layer samples. We preliminarily attribute this behavior to changes in the metal-ligand covalency with magnetic state. Our results clarify the magneto-optical response of CrI₃ and identify covalency as a central mechanism for the brightening and field tunability of spin-forbidden multiplet excitations.

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I. INTRODUCTION

Chromium trihalides (CrX₃, *X* = Cl, Br, I) are van der Waals layered magnetic insulators [1]. CrBr₃ and CrI₃ are historically important as they are among the first known examples of insulating ferromagnets [1–7]. Thus, there has been significant effort in understanding the magneto-optical spectra of these materials [3–5,8–14]. In the more ionic cases of CrBr₃ and CrCl₃, the optical range excitations ($E \simeq 1.5 \rightarrow 3$ eV) are well described by Cr³⁺ (*3d*³) *dd* excitations [5,9,12,13] within ligand field theory [15],

followed by ligand-to-metal charge-transfer (LMCT) transitions at higher energy (> 2.6 and > 3.6 eV for *X* = Br and Cl, respectively) [9–11,16]. Meanwhile, the reduced charge-transfer energy and increased metal-ligand covalency for CrI₃ challenges such assignments, with both LMCT and *dd* transitions overlapping in the near-infrared and visible energy range ($1.5 \rightarrow 3.0$ eV) [14]. The optical spectra and electronic energy scales of CrI₃ have received relatively less attention until recently [17–28].

CrX₃, in particular CrI₃, are of strong contemporary interest in the context of two-dimensional (2D) magnetism. CrI₃ is an easy-axis ferromagnet (FM) ($T_C \sim 61$ K [17]) that is exfoliable and maintains long-range intralayer FM order down to the single-layer limit [18,29]. These unique features have enabled the study of emergent magnetic properties in 2D, including the layer-dependent magnetic order where few-layer samples become A-type antiferromagnets (AFMs) due to structurally induced changes in the interlayer magnetic exchange [17,18,30–32]. The highly tunable interlayer exchange has been key for studies of novel magnetic states in, e.g., moiré heterostructures [33–35].

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Central to many of these studies are magneto-optical effects (e.g., magnetic circular dichroism [MCD] and the magneto-optic Kerr effect [MOKE]), which provide the primary methods to probe the magnetic order of atomically thin samples. Modern works favor the interpretation of magneto-optical effects within band structure plus Bethe-Salpeter equation (BSE) approaches [23,36–38]. However, the connection between BSE and the ligand field and molecular orbital theory that appropriately describes $\text{CrBr}_3/\text{CrI}_3$ is not transparent, leading to inconsistencies in the interpretation. Meanwhile, the magneto-optical spectra have not been systematically investigated in CrI_3 , and it is unknown how they depend on layer number and the underlying magnetic state. Thus, despite the importance for probing magnetic order [18] and the mechanisms of photoinduced magnetic effects [29,39–41], an understanding of the magneto-optical response of CrI_3 is currently incomplete.

There has also been recent interest in spin-forbidden excitations contributing to the magneto-optical response. This is exemplified by the spin-flip ${}^2E_g/{}^2T_{1g} \rightarrow {}^4A_{2g}$ luminescence in CrPS_4 [42–44], commonly observed in Cr^{3+} compounds [5,9,13,45–50], and the sharp ${}^1A_{1g} \leftrightarrow {}^3A_{2g}$ excitations in optical absorption and luminescence of NiPS_3 [51–58] and the nickel dihalides [51,59–65]. Spin-forbidden excitations correspond to a change the total spin (S) of the transition-metal ion and are associated with a specific type of dd excitation with energies determined by Hund’s coupling [66–68]. Such excitations are of interest due to their characteristically small linewidths [67] and the proposed connection of their optical cross section to magnetic order [52,59–61,69] or inversion symmetry breaking [44,55,63]. Thus, such excitations may provide a pathway to optically probe the magnetic properties of 2D materials. However, the generality, properties, and mechanisms for enabling spin-forbidden transitions have not been clarified. In particular, such excitations have not been identified in CrI_3 , in part due to the complexity of the optical spectra.

In this work, we report MCD spectroscopy and Cr L_3 -edge resonant inelastic x-ray scattering (RIXS) studies of CrI_3 . MCD spectroscopy measurements reveal the presence of both spin-allowed (${}^4A_{2g} \rightarrow {}^4T_{2g}/{}^4T_{1g}$) and unreported spin-forbidden (${}^4A_{2g} \rightarrow {}^2E_g/{}^2T_{1g}$) excitations near the lowest allowed LMCT band edge. The excitations are assigned through RIXS measurements, charge-transfer multiplet (CTM) calculations, and chemical trends in the CrX_3 series. We further use the high sensitivity of MCD spectroscopy to study the thickness dependence of the optical spectra. These data demonstrate that the spin-forbidden excitations remain robust down to the monolayer limit. We further report a significant field dependence of the MCD spectrum in few-layer AFM samples. Through comparison with the MCD spectrum of CrBr_3 , we preliminarily associate these observations with an increased

Cr-X covalency that is tunable by both ligand and the magnetic state. These results yield a consistent interpretation of the magneto-optical spectra of the chromium trihalides and strongly suggest the importance of metal-ligand covalency for the mechanisms of brightening and tuning spin-forbidden multiplets in correlated insulators.

II. RESULTS

A. Magneto-optical spectra of bulk CrI_3

We begin by discussing the MCD [$\text{MCD}(\epsilon)$] and reflectance [$R(\epsilon)$] spectra versus photon energy (ϵ) in bulk CrI_3 recorded in backscattering geometry at normal incidence [Fig. 1(a)] (for experimental details; see Supplemental Material [70]). Bulk spectra were recorded on an approximately 20-nm-thick flake double encapsulated with $h\text{-BN}$ [Fig. 1(b)]. At $T = 1.75$ K, we first recorded an MCD hysteresis loop at $E = 1.959$ eV and $\vec{B} \parallel \hat{c}$ along the easy axis of CrI_3 , confirming FM behavior with coercive field $B_c \sim 250$ mT [Fig. 1(c)]. $\text{MCD}(\epsilon)$ and $R(\epsilon)$ are reported in Figs. 1(d) and 1(e), respectively. The

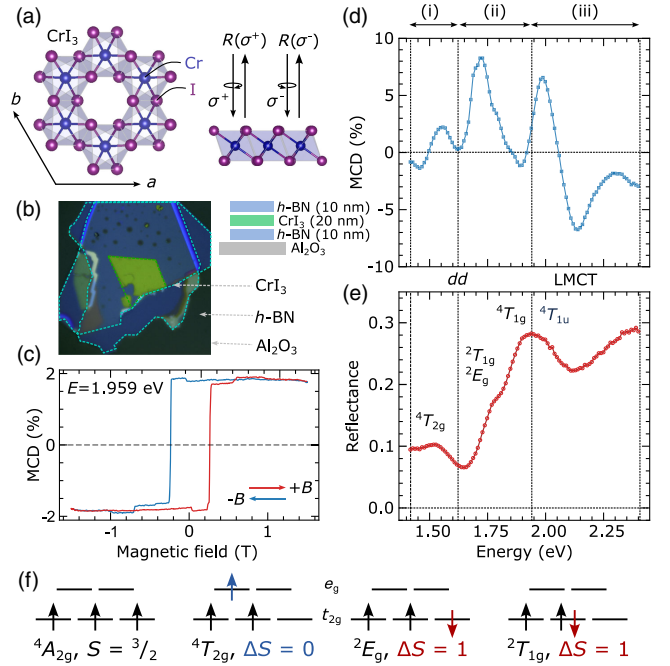


FIG. 1. (a) Planar crystal structure of CrI_3 and MCD measurement geometry with σ^+/σ^- polarizations incident along the $\hat{c}$ axis. (b) Approximately 20-nm-thick CrI_3 flake (green outline) double encapsulated by approximately 10-nm $h\text{-BN}$ (blue) transferred onto an Al_2O_3 substrate for optical measurements. (c) MCD hysteresis loop at $E = 1.959$ eV and $T = 1.75$ K. (d) MCD and (e) reflectance [$R(\epsilon)$] spectra at $T = 1.75$ K. The different spectral regions (i)–(iii) and peak assignments are indicated (see text for details). (f) Schematics of the ground and lowest excited-state multiplets for the Cr^{3+} (d^3) ion in octahedral symmetry. The crystal structure in (a) is generated by VESTA [76].

MCD spectra are recorded at $B = 0$ T and antisymmetrized with respect to the magnetic state by applying $\pm B_c$ and returning to $B = 0$ T.

We observe several prominent features in the MCD(ϵ) and $R(\epsilon)$ measurements including transitions at the following energies: (i) $E = 1.4 \rightarrow 1.62$ eV, (ii) $1.62 \rightarrow 1.94$ eV, and (iii) $1.94 \rightarrow 2.4$ eV [Figs. 1(d) and 1(e)]. The lowest energy feature in MCD(ϵ) and $R(\epsilon)$ agrees with the expected ${}^4A_{2g} \rightarrow {}^4T_{2g}$ Cr^{3+} multiplet excitation in octahedral (O_h) crystal field, representing a spin-allowed ($\Delta S = 0$) $t_{2g} \rightarrow e_g$ interorbital transition [19] [Fig. 1(f)]. At higher energies, a larger reflectance band edge is observed beginning around 1.7 eV and peaking near 1.94 eV. The peak near 1.94 eV is an LMCT transition [14,16,19] mixed with the higher-energy spin-allowed ${}^4T_{1g}$ multiplet as shown below.

Preceding the LMCT feature, we observe a prominent multi-peaked excitation from $1.65 \rightarrow 1.90$ eV in MCD(ϵ). Previous optical measurements have observed excitations in this energy range but without assignment [19–22]. An enlargement of this spectral region is shown in Fig. 2(a), showing multiple peaks between 1.650 and 1.850 eV which appear qualitatively sharper than the other features in the MCD spectrum. A corresponding reflectance signal is also observed in a similar energy range [Figs. 2(c) and 2(d)]. The lowest-energy peaks in MCD(ϵ) agree well with the expected energy of ${}^2E_g/{}^2T_{1g}$ spin-forbidden ($\Delta S = 1$) transitions [Fig. 1(f)], which are commonly observed in the luminescence of strong-field octahedrally coordinated (O_h) Cr^{3+} ions or color centers [45,46,50], while the higher-energy peaks resemble two-phonon or magnon sidebands [5,9,13,50,59,61]. The precise assignment of all features in this spectral region (in the bulk) is complicated by the presence of both resonance and antiresonance line shapes in MCD spectra and will be substantiated by additional measurements below. However, these results reveal sharp excitations near 1.7 eV and show that MCD spectroscopy is effective to resolve them from the more strongly allowed LMCT bands.

We proceed with temperature dependence of MCD(ϵ) and $R(\epsilon)$ as reported in Figs. 2(b) and 2(d). The zero-field MCD signal continuously reduces to zero with increasing T up until $T_C \simeq 60$ K, as expected with the vanishing ordered magnetization [1,8]. In the $R(\epsilon)$ measurements [Fig. 2(d)], a moderate temperature dependence is observed for the 1.8 eV peak, which broadens and eventually merges with nearby excitations with increasing temperature. This fine structure has been associated with either a bright exciton from BSE calculations or the ${}^4T_{1g}$ (spin-allowed) dd excitation [14,19,22,36]. We examine this energy region more closely by fitting the ${}^4T_{2g}$ and LMCT transitions with Gaussian peaks and subtracting them from the signal to report the additional 1.8 eV spectral weight in Fig. 2(c). A close correspondence between this excitation with the

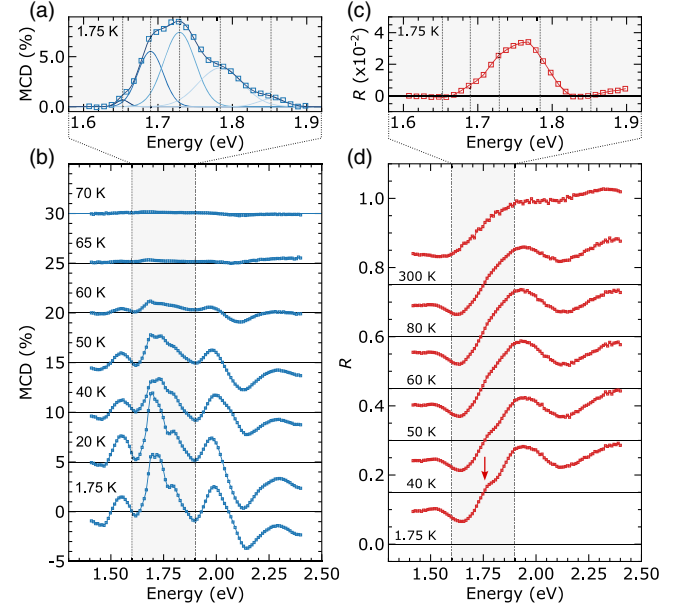


FIG. 2. (a) Enlargement of the MCD spectrum in the energy range 1.6–1.9 eV at $T = 1.75$ K on the 20-nm sample in Fig. 1. Blue squares are data, and the black line is a fit with a linear baseline subtracted and Gaussian fit components shown in blue. (b) Temperature dependence of the MCD spectrum showing the disappearance across $T_C \simeq 60$ K, as expected. (c) Enlargement of the shoulder of $R(\epsilon)$ at $T = 1.75$ K in the energy range 1.6–1.9 eV with nearby spectral components subtracted from a minimal Gaussian peak fit. (d) Temperature dependence of $R(\epsilon)$. Vertical dashed lines in (a) and (c) are the energies of the fit components from the MCD spectrum in (a), and vertical lines in (b) and (d) denote the energy region 1.6–1.9 eV highlighted in (a) and (c). Red arrow in (d) highlights the T -dependent fine-structure component near 1.8 eV.

sideband region of the $\Delta S = 1$ transitions observed in MCD [Fig. 2(a)] is noted, and we assign this feature accordingly. This assignment may explain the significant vibronic coupling observed in Raman measurements with incident energy tuned to this spectral region [22].

B. Cr L_3 -edge RIXS measurements

In order to bolster the assignments of the excitations in the optical spectra, we performed RIXS measurements at the Cr L_3 -edge ($2p_{3/2} \rightarrow 3d$) on bulk chemical-vapor-transport-grown single crystals of CrI_3 . The distinct selection rules of the two-dipole transition RIXS process alongside the spin-orbit coupling (SOC) in the core levels allow direct sensitivity to both spin-allowed and spin-forbidden dd excitations of transition-metal ions [77]. Furthermore, local cluster models based on ligand field or charge-transfer multiplet theory are able to quantitatively capture the excitation energies as well as their intensity and incident-energy dependence [78,79], providing additional information for peak assignment.

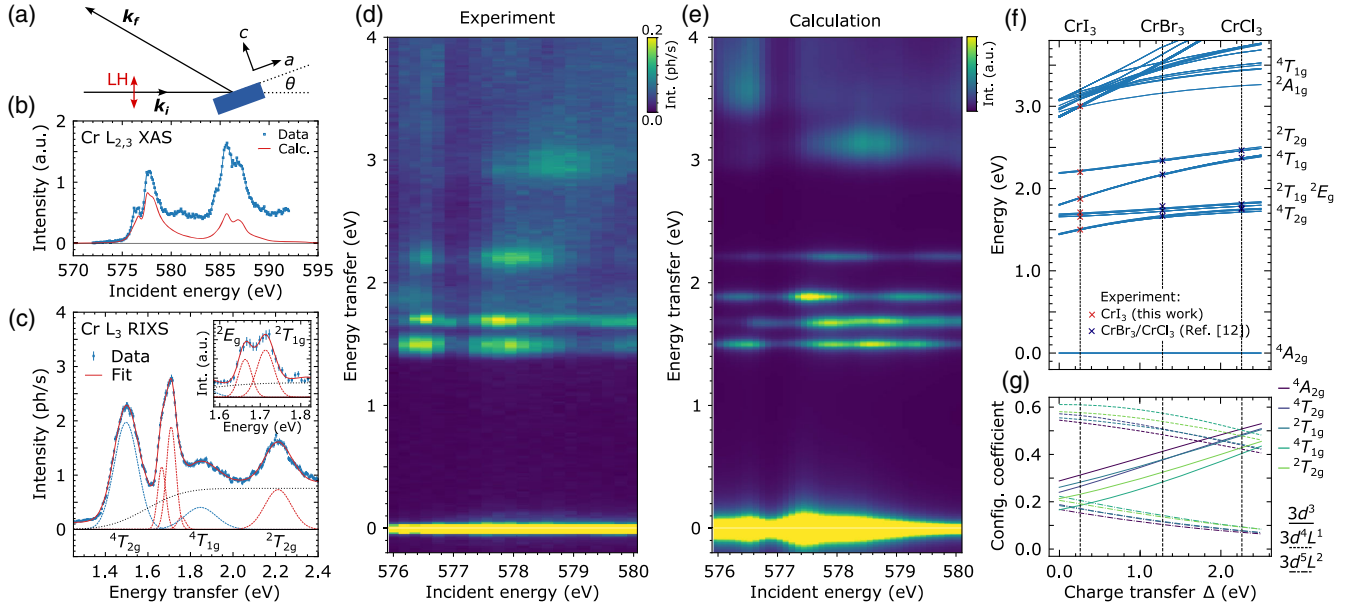


FIG. 3. (a) Experimental geometry for RIXS measurements. (b) Cr $L_{2,3}$ -edge XAS measurements in PFY (blue) at $\theta = 90^\circ$ with the calculated XAS from CTM modeling overlaid (red; see text). (c) Cr L_3 -edge RIXS spectrum integrated over incident energy from the (d) energy-dependent RIXS map. In (c), blue squares are the experimental data with individual Gaussian fit components to $\Delta S = 0$ (blue) and $\Delta S = 1$ (red) excitations shown. The black line is a steplike background to account for fluorescence. Inset: an enlargement of the region 1.6–1.8 eV recorded in a higher resolution ($\Delta E \simeq 22$ meV) at $E = 577.5$ eV, highlighting the ${}^2E_g/{}^2T_{1g}$ excitations. Comparison between (d) experimental and (e) calculated RIXS maps recorded at $T = 40$ K, $\theta = 15^\circ$, and $2\theta = 150^\circ$ with incident π polarization. The calculation considers the same experimental geometry and polarization conditions. (f) Energy-level diagram as a function of the charge-transfer gap (Δ) based on optimized fits to the lowest-energy multiplet excitations in CrI_3 , CrBr_3 , and CrCl_3 . The energies for CrBr_3 and CrCl_3 are from optical absorption in Ref. [12] (purple crosses), and the CrI_3 values are determined from RIXS measurements in panel (c) (red crosses). (g) Evolution of the $3d^3$, $3d^4\bar{L}^1$, and $3d^5\bar{L}^2$ configurational weights resolved to the ground- and lowest excited-state multiplets as a function of Δ . In (f) and (g), the ionic crystal field splitting ($10Dq$) and the nephelauxetic reduction (β) are covaried with Δ based on interpolation of the optimized values as a function of the halogen (see text and Table I).

RIXS measurements were performed at the 2-ID (SIX) beamline at the National Synchrotron Light Source II [80], with a resolution of $\Delta E \sim 27$ meV and at a temperature of $T = 40$ K. We utilized a fixed scattering geometry with $2\theta = 150^\circ$ scattering angle and incident linear horizontal (π) polarization [Fig. 3(a)]. The samples were handled and cleaved inside an N_2 environment before loading into the high-vacuum sample chamber.

Figure 3(b) shows the $L_{2,3}$ -edge x-ray absorption spectroscopy (XAS) spectrum of CrI_3 recorded in partial fluorescence yield (PFY) with π incident polarization at normal incidence ($\theta = 90^\circ$). We measured incident-energy-dependent RIXS maps across the Cr L_3 -edge at fixed $\theta = 15^\circ$ with incident π polarization [Fig. 3(d)]. We observe a sequence of sharp Raman-like excitations in the energy range $1.5 \rightarrow 3.0$ eV. The excitations in the $1.3 \rightarrow 2.4$ eV energy range can be observed more clearly in Fig. 3(c) where we report the incident-energy-integrated RIXS spectrum (from 576.0 to 580.0 eV). We fit the sharp features and identify excitations at energies of 1.497 eV (131 meV), 1.665 eV (45 meV), 1.709 eV (53 meV), 1.753 eV (45 meV), 1.846 eV (175 meV), and 2.211 eV (147 meV) with the values in parentheses representing the

full width at half maximum (FWHM) from Gaussian fits. The doublet peak near 1.7 eV is qualitatively sharper than the other excitations similar to observations in MCD [Fig. 2(a)]. A higher-resolution measurement with $\Delta E = 22$ meV at incident energy $E = 577.5$ eV is shown in Fig. 3(c) (inset), showing a well-resolved doublet excitation with energies (FWHM) of 1.664 eV (38 meV) and 1.712 eV (48 meV). Each feature below 2.0 eV in the RIXS spectrum has a corresponding excitation in MCD(ϵ) and $R(\epsilon)$ measurements (Figs. 1 and 2).

C. CrX_6 cluster calculations

To assign the features in the RIXS and optical experiments, we utilize CTM theory and model the Cr $L_{2,3}$ -edge XAS and RIXS spectra using QUANTY [79,81]. The large Cr-I covalency [64] necessitates the consideration of charge-transfer effects including the $3d^3$, $3d^4\bar{L}$, and $3d^5\bar{L}^2$ electronic configurations in the calculations, where $\bar{L}$ corresponds to a hole in the ligand orbitals ($\text{I-}5p$), discussed more below. We utilize the standard procedure [79] and consider a single CrI_6 cluster with a basis consisting of the five Cr-3d orbitals and the symmetrized (bonding) I-5p molecular orbitals of e_g and t_{2g} symmetry.

We consider the case of O_h symmetry in the main text. The slight trigonal distortion in CrI_3 [82,83] plays a minor role for the present results and is considered in more detail in the Supplemental Material [70].

The parameters in the cluster model include the Cr $3d$ - $3d$ and $2p$ - $3d$ Coulomb interactions (Slater integrals), the Cr $2p$ and $3d$ SOC, the O_h crystal field splitting ($10Dq$), the hybridization between the metal and ligand e_g and t_{2g} states, the charge-transfer gap (Δ), and the Coulomb repulsion in the initial and intermediate RIXS states (U_{dd} and U_{pd} , resp.). The key parameters for the present discussion are the crystal field splitting ($10Dq$), the charge-transfer gap (Δ), and the nephelauxetic reduction (β), which represents the reduction of Slater integrals from atomic values. Further parameter details are provided in Supplemental Material (Methods) [70].

The optimized results of the calculations for CrI_3 are shown in Fig. 3(b) for the XAS spectrum (red line) with the corresponding RIXS map shown in Fig. 3(e). The parameters are reported in Table I. We find an excellent agreement for both datasets, including the energy of all observed Raman-like excitations in the RIXS profile and their incident energy dependence. The relative intensity deviations between the Cr L_3 pre- and main edge in RIXS, as well as the L_2/L_3 branching ratio in XAS, are attributable to self-absorption effects [77]. We also note postedge features in the Cr $L_{2,3}$ -edge XAS ($E \simeq 582$ and 593 eV), which are likely charge-transfer satellites similar to observations in Ni^{2+} systems [52,58,64] and are captured by the CTM calculations (see Supplemental Material [70]). From these calculations, the dd excitations in RIXS can be assigned as ${}^4T_{2g}$ (1.5 eV), 2E_g (1.664 eV), ${}^2T_{1g}$ (1.712 eV), ${}^4T_{1g}$ (1.85 eV), ${}^2T_{2g}$ (2.21 eV), and ${}^4T_{2g}$ (3.0 eV). Most importantly, the doublet excitation revealed in MCD measurements near 1.7 eV (Figs. 1 and 2) corresponds to the spin-flip $\Delta S = 1$ intraconfigurational ${}^2E_g/{}^2T_{1g}$ multiplets.

To substantiate the accuracy of the CTM model, we take the observed dd excitation energies for CrBr_3 and CrCl_3 below 3 eV from the available optical literature [12] and fit the excitations to the same model. The optimized parameters for each ligand are reported in Table I with the corresponding energy-level diagram as a function of Δ shown in Fig. 3(f). A satisfactory fit for all ligands is achieved for the multiplets below 3 eV. The fitted values of

Δ are systematically lower than the results from previous x-ray photoelectron spectroscopy (XPS) analysis [84], since Δ reported here refers to the center of the configurations and not with respect to the ${}^4A_{2g}$ ground state after including multiplet coupling and the crystal field [85]. However, the trend of Δ we optimize across the series is in good agreement with reports from both XPS [84] and optical spectroscopy of the charge-transfer band edge [11,16].

To examine the role of charge transfer, we extract the configurational contributions to the ground- and lowest-energy excited states versus Δ in Fig. 3(g). This analysis shows an excitation-dependent mixing between the ionic and charge-transfer configurations, with significant $3d^5\bar{L}^2$ configurational weight observed, particularly for CrI_3 ($\Delta = 0.26$ eV). Restricting the model to only the $3d^3$ and $3d^4\bar{L}$ configurations results in inaccurate fits to the extreme case of CrI_3 , required significantly smaller values of Δ for all ligands, and yields disagreement with the RIXS and XAS spectra [70]. Similarly, the atomic ($3d^3$) results (e.g., Tanabe-Sugano diagrams [15,28]) are not able to reproduce the experimentally observed energy levels in CrX_3 [70]. Thus, configuration interactions with the explicit inclusion of charge-transfer states are crucial to describe the observed excitations (for additional information on the results using different configuration bases, see Supplemental Material [70]). Some excitations have an overestimated intensity in the CTM calculation, in particular, the ${}^4T_{1g}$ excitation [Figs. 3(d) and 3(e)]. This overestimation correlates with the excitation-dependent contribution of the charge-transfer configurations [Fig. 3(g)]. We associate this disagreement between the experimentally-observed and calculated intensities with the effects of the ligand bandwidth which is not included in the calculations. This suggests that single cluster models are at the margins of applicability in the case of CrI_3 with band-structure effects becoming important [23].

We finally address the relationship between the charge-transfer configurations and the LMCT excitons observed in optical experiments (Fig. 1) [11]. The lowest-energy dipole-allowed transitions in optics are from the nonbonding t_{1u}/t_{2u} molecular orbitals to the (antibonding, metal-centered) e_g^* states with term ${}^4T_{1u}$ [16]. Being nonbonding, the t_{1u} and t_{2u} ligand orbitals are (by construction) absent from the cluster model which considers only the bonding e_g and t_{2g} ligand orbitals [79]. Therefore, the LMCT excitons observed at 1.94 and 2.8 eV in optics [14,16,19] are not included in the model and are distinct from the dd transitions observed and calculated at 2.21 and 3.0 eV. The LMCT excitons are more strongly dipole allowed and likely obscure the observation of these higher-energy dd excitations in optics. Conversely, the ${}^4T_{1u}$ excitations are not clearly observed in RIXS, but the multiplet assignments show a near degeneracy between the experimentally observed LMCT exciton and the ${}^4T_{1g}$ dd excitation, confirming the assignments in Fig. 1.

TABLE I. Optimal cluster model parameters for CrX_3 for $X = \text{I, Br, Cl}$ considering the $3d^3$, $3d^4\bar{L}$, and $3d^5\bar{L}^2$ configurations (see text for details).

X	β	$10Dq$ (eV)	Δ (eV)
I	0.906	1.300	0.26
Br	0.916	1.445	1.28
Cl	0.925	1.500	2.27

D. Layer-dependent magneto-optical spectra

Having established the origin of the optical excitations of bulk CrI_3 , we now utilize the high sensitivity of MCD spectroscopy to the spin-forbidden $^4A_{2g} \rightarrow ^2E_g/^2T_{1g}$ excitations to study their evolution with sample thickness. Layer-dependent magneto-optical spectra are reported in Fig. 4(a), including 1L, 2L, 4L, 5L, and an additional exfoliated bulk sample (approximately 100-nm thickness). All spectra are recorded from samples on Al_2O_3 substrates. Each spectrum is taken at sufficiently large magnetic field to saturate the magnetization, which depends on the layer number due to the AFM interlayer exchange coupling in few-layer CrI_3 [18]. The excitation energies and the MCD magnitude do not change significantly with increasing field past full saturation [70]. Thus, the spectra in Fig. 4 are directly comparable despite the different externally applied magnetic fields. The few-layer data are qualitatively distinct from the bulk due to finite-thickness (thin-film) effects in the bulk sample leading to antiresonance line shapes, e.g., for the $^4T_{2g}$ excitation in MCD [Figs. 1(d) and 4(a)]. The few-layer data instead closely resemble previously reported bulklike MCD spectra in transmission [21]. Despite the details of the spectral shape, the key excitations in the bulk (Fig. 1) are also observed in all thicknesses down to the monolayer, including the $\Delta S = 1$ excitations near 1.7 eV.

We extract the layer-dependent excitation energies in Fig. 4(b). A small blueshift (redshift) of the $^4T_{2g}/^4T_{1u}$ ($^2E_g/^2T_{1g}$) excitations of < 30 meV from bulk to

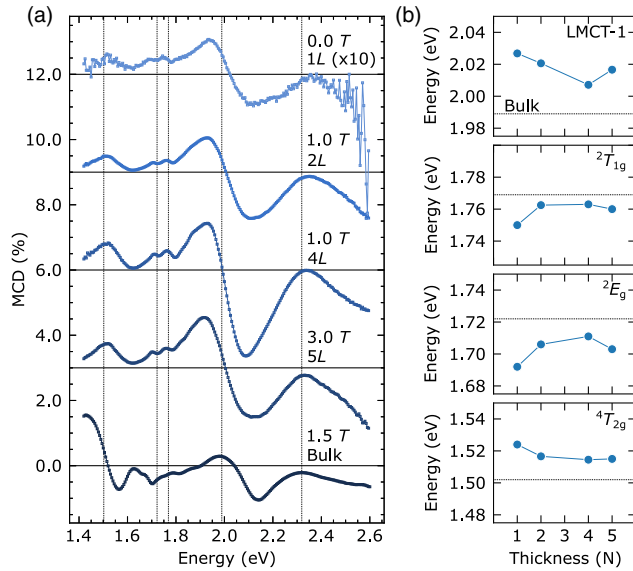


FIG. 4. (a) Thickness-dependent MCD spectra at $T = 1.75$ K for 1L, 2L, 4L, 5L, and exfoliated bulk (thickness approximately 100 nm). Spectra are recorded at the indicated field to achieve the fully saturated FM state in each sample. Vertical lines are guides to the eye. (b) Thickness dependence of the energies for the principal dd and LMCT transitions. Horizontal dashed lines are the bulk values from optical measurements.

monolayer is observed, respectively. This could be due to small renormalization of Δ , $10Dq$, and/or the electronic correlations with thickness as previously argued in other 2D magnets like NiPS_3 [86,87], and agrees with the LMCT transition shift observed at room temperature [24], though with a smaller magnitude in our data. Crucially, the magneto-optical spectra and the spin-forbidden multiplets are robust down to the monolayer limit.

As noted in the bulk (Fig. 2), the $^2E_g/^2T_{1g}$ peaks in MCD are systematically higher in energy compared to RIXS [Fig. 3(c)], with an energy difference of around 40–50 meV. This could be due to a difference in MCD and absorption, where the position of maximum dichroism does not necessarily align with the fundamental energy of the underlying excitation. Alternatively, these peaks could be two-phonon or magnon sidebands [48,50,88] consistent with the magnon and phonon dispersion bandwidth of approximately 20 and 30 meV [89,90], respectively. In particular, two-magnon sidebands are common to the spin-forbidden excitations of Cr^{3+} systems [48]. This may partially explain their large contribution in MCD and their temperature-dependent broadening above T_C [Fig. 2(d)]. Close inspection (Fig. 5) shows additional spectral weight near 1.65 eV. This may represent the fundamental (zero-boson) 2E_g excitation, as this aligns more closely with the

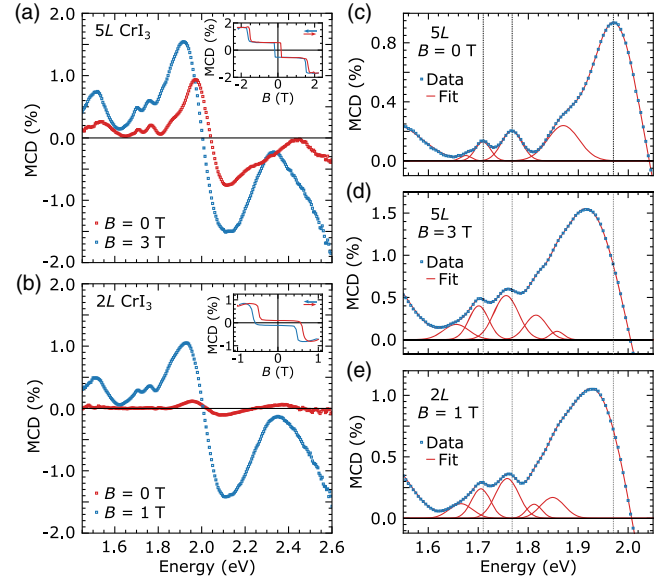


FIG. 5. Dependence of the MCD spectrum on the magnetic state in few-layer CrI_3 at $T = 1.75$ K. (a) Antisymmetrized MCD spectrum for 5L CrI_3 at $B = 0.0$ T (red) and $B = 3.0$ T (blue), respectively. (b) Antisymmetrized MCD spectrum for 2L CrI_3 at $B = 0.0$ T (red) and $B = 1.0$ T (blue), respectively. Insets to (a) and (b) are the respective hysteresis loops recorded with fixed $E = 1.959$ eV. Fits to the (1.6–2.0)-eV region highlighting the $\Delta S = 1$ excitations for (c) 5L CrI_3 at $B = 0.0$ T, (d) 5L at $B = 3.0$ T, and (e) 2L at $B = 1.0$ T. Blue squares are the experimental data, and red solid lines indicate the total and individual fit components.

2E_g peak in RIXS [Fig. 3(c)], though higher-resolution optical studies would be required to ascertain whether any sharp zero-boson $\Delta S = 1$ excitations are present. However, we highlight that the linewidths of the ${}^2E_g/{}^2T_{1g}$ excitations in optics (approximately 27 meV) and in RIXS (approximately 38 and 48 meV) are both not resolution limited. This suggests that even the fundamental multiplet excitations are intrinsically broad.

E. Magnetic-field dependence

The layer-dependent ground state of few-layer CrI_3 offers additional opportunities to study the effects of the magnetic state on the optical spectrum that are inaccessible in bulk. While the bulk is FM, the weak interlayer AFM coupling of few-layer CrI_3 allows a switching between layered AFM and FM states through metamagnetic transitions [18,30–32]. We thus studied the magnetic-field-dependent MCD spectrum of 5L and 2L CrI_3 at $T = 1.75$ K shown in Figs. 5(a) and 5(b), respectively. The insets show the hysteresis at fixed $E = 1.959$ eV for each sample, confirming the field-induced transition from AFM to FM stacking configurations at $B_c(5L) \sim 1.8$ T and $B_c(2L) \sim 0.6$ T. The 5L sample shows a remnant magnetization at zero field due to the odd layer number, while the bilayer is nearly compensated at $B = 0$ T, consistent with previous reports [91].

Figure 5(a) compares the MCD spectrum at $B = 0$ T and $B = 3$ T in the 5L sample. Besides an increased overall MCD magnitude at higher field due to the increased net magnetization, qualitative differences are observed in the MCD spectrum in the AFM and FM coupled states. This includes an apparent shift of the LMCT transitions to lower energy, with a corresponding (weaker) redshift of the ${}^2E_g/{}^2T_{1g}/{}^4T_{2g}$ multiplets. For the bilayer [Fig. 2(b)], the zero-field MCD contrast is small across the full spectral range, while a similar field-induced redshift of the LMCT transition is observed. We focus on the region of the LMCT transition and the $\Delta S = 1$ excitations in Figs. 5(c)–5(e) and fit the MCD spectrum. Based on these fits, we quantify an effective-field-induced redshift of approximately 8 and 10 meV for the 2E_g and ${}^2T_{1g}$ excitations, respectively, and an approximately 20- and 50-meV redshift of the ${}^4T_{2g}$ and LMCT peaks, respectively, from the AFM ($B = 0$ T) to FM ($B > 1.8$ T) states. Meanwhile, the MCD spectrum in the FM state of both 2L and 5L [Figs. 5(d) and 5(e)] are in close relative agreement.

These results suggest either a modification of the excitation energies or a large redistribution of CD contrast induced by the change in magnetic state in CrI_3 . This is nontrivial, as it is commonly assumed that MCD at fixed probe energy is proportional to the net magnetization, which is implicit in the interpretation of magnetic properties. An energy shift induced by the metamagnetic transition could be consistent with either a decrease of the

charge-transfer gap or an increase of the Cr-I hybridization based on our CTM analysis [Fig. 3(f)]. Indeed, a modified Cr-I overlap is evidenced by structural changes across the metamagnetic transition in 2L CrI_3 inferred by Raman spectroscopy [30]. This interpretation would be consistent with the experimental observation of magnetic-state-dependent optical spectra in, e.g., Ni_3TeO_6 [92], $\text{Ni}_3\text{V}_2\text{O}_8$ [93], and CrSBr [94]. Separately, we also observe an increase in the strength of the dd excitations relative to the LMCT exciton in the FM state [Figs. 5(c) and 5(d)]. Thus, increased hybridization induced by the change in magnetic order may contribute to optically brightening these transitions. Alternatively, this effect may induce an apparent energy shift by redistributing CD contrast between distinct excitations or unresolved fine structure. Direct field-dependent optical absorption measurements in few-layer CrI_3 would be required to definitively support the underlying mechanism. However, we recall that MCD spectroscopy is critical to clearly resolve the overlapping dd and charge-transfer peaks near 1.7 eV.

To substantiate the proposed role of metal-ligand covalency, we compare the MCD spectrum of FM 5L CrI_3 with that of thin bulk (approximately 10 nm thick) FM CrBr_3 in Fig. 6. The spectra are recorded in the fully saturated FM state of each sample and are directly comparable since no significant changes to the MCD magnitude or excitation energies are observed for magnetic fields exceeding saturation for either CrI_3 or CrBr_3 [13,70]. This comparison effectively tunes the covalency through ligand substitution, which is smaller in Br due to the smaller ionic radius. All dd excitations are a factor > 6 weaker in CrBr_3 —relative to the primary LMCT transition—compared to CrI_3 , supporting the possible role of increased metal-ligand covalency in CrI_3 in the enhanced optical brightness. Below 2.2 eV, only spin-allowed transitions are observed in CrBr_3 , and the ${}^2E_g/{}^2T_{1g}$ peaks expected at similar energies to CrI_3

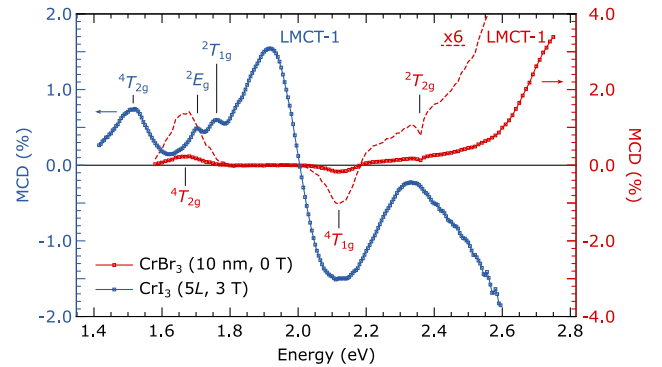


FIG. 6. Comparison between the MCD spectrum in thin layers of CrI_3 (blue, left axis) and CrBr_3 (red, right axis), both within the fully saturated ferromagnetic state. The dashed red line is multiplied by a factor of 6 for comparison. Individual excitations based on multiplet calculations in Fig. 3 are indicated for each compound.

[Fig. 3(f)] [12] are not clearly observed. However, a higher-energy spin-forbidden ${}^2T_{2g}$ transition is observed near 2.33 eV [Fig. 3(f)] [5].

Thus, the optical cross section of the intraconfigurational $\Delta S = 1$ transitions may be more sensitive to ligand hybridization compared to the $\Delta S = 0$ transitions. This could be due to reduced Franck-Condon coupling for the intraconfigurational transitions [88], an alternative brightening mechanism primarily active only for interconfigurational excitations [15]. Meanwhile, single-ion mechanisms for relaxing the parity and spin-selection rules, such as static odd-parity trigonal field, SOC-induced mixing of spin-forbidden and spin-allowed terms, or nonelectric-dipole transitions [12], cannot be reconciled with the large observed cross sections or the ligand-dependent trends [70]. Alternatively, ligand SOC may be effective for relaxing the spin selection rule of the $\Delta S \neq 0$ transitions, an effect which would increase along with increased ligand atomic number and correlate with the increase in hybridization. Notably, ligand SOC in combination with the effect of the net spin exchange may provide a mechanism for coupling the $\Delta S = 1$ transitions to the magnetic order or short-range magnetic correlations [12,70], possibly explaining an increase of intensity across T_C [Fig. 2(d)].

III. DISCUSSION

A consistent interpretation of these observations, including the ligand and field dependence of the multiplet energies and their optical brightness, relates to the degree of hybridization between the metal and ligand states. In the ionic limit, dd transitions are parity forbidden and weakly optically allowed. As hybridization and covalency increase, the dd excitations become mixed with the ligand p states. This has the effect of modifying their energies through configuration interactions [Fig. 3(f)] and simultaneously increasing their optical cross section (Figs. 5 and 6) through the relaxation of both the parity and spin-selection rules, with the relaxation of the spin selection rule likely being due to increased ligand SOC introduced by heavier halogen ligands (e.g., I).

While the excitations of CrI_3 can be accurately mapped to Cr^{3+} dd excitations that get modified by charge transfer, the ligand orbitals in real solids form dispersive bands. The large contribution of charge-transfer configurations in the case of CrX_3 likely signals an importance of these bandlike states. This conclusion is consistent with quasiparticle self-consistent $G\hat{W}$ results, suggesting that ligand covalency in CrX_3 is the primary brightening mechanism of the dd excitations [23], though such calculations did not capture the $\Delta S = 1$ excitations of focus here [95]. The importance of bandlike states is also evidenced by the enhanced photoconductivity at dd transitions in highly covalent systems [65,96,97] and are likely responsible for their momentum dependence [98], as recently observed in

the nickel dihalides [64] and NiPS_3 [58]. Notably, the ${}^3A_{2g} \rightarrow {}^1A_{1g}$ spin-forbidden excitations in these Ni^{2+} systems follow similar trends of optical brightness with ligand covalency [7,51,59,61,62,99].

We finally address the linewidths of the spin-forbidden excitations in CrI_3 . The small linewidths generally observed for spin-forbidden multiplets is a property that has attracted significant interest [52–54,58,63,64]. For example, the prominent ${}^3A_{2g} \leftrightarrow {}^1A_{1g}$ transition in NiPS_3 is nearly resolution limited in both RIXS and optical measurements [52–54]. Meanwhile, the ${}^2E_g/{}^2T_{1g}$ peaks in CrI_3 are broader than experimental resolution in both techniques, but remain sharper than the spin-allowed transitions (e.g., ${}^4T_{2g}$). This distinction in linewidths is a general property related to Franck-Condon effects for which the crucial ingredient is the conservation of the ground-state orbital configuration [67,68,88], as also supported by our RIXS and optical measurements.

The increased linewidth of the intraconfigurational excitations in CrI_3 (approximately 27 meV) compared to several Ni^{2+} systems (nearly resolution limited for the ${}^1A_{1g}$ excitation) could be due to either the higher excitation multiplicity (4 and 6 for 2E_g and ${}^2T_{1g}$, respectively) or a larger contribution of bandlike ligand states. Indeed, a distinct linewidth is observed for the 1E_g and ${}^1A_{1g}$ states in the nickel dihalides, possibly due to their distinct multiplicities [64], which allows an (unresolved) broadening from fine structure in reduced symmetry. In addition, while the ${}^1A_{1g}$ excitations in NiCl_2 , NiBr_2 , and NiPS_3 are nearly resolution limited, the corresponding excitation in NiI_2 is broader [63,64], similar to the present results in CrI_3 . One common feature is the proximity to the band gap and the increased hybridization with ligand states which may simultaneously brighten and broaden the excitation. This observation may be characteristic of the I $5p$ states which are more spatially extended and have larger bandwidth compared to, e.g., Br $4p$ or S $3p$.

A primary goal for future studies should be to quantitatively describe the microscopic relationship between the optical brightness, excitation linewidth, and momentum dependence of dd excitations and their interdependence with ligand electronegativity and bandwidth. Such efforts promise to reveal novel and emergent properties of the excitations in intermediate systems simultaneously exhibiting both strong correlations and covalency.

IV. CONCLUSION

We have reported the observation of ${}^4A_{2g} \rightarrow {}^2E_g/{}^2T_{1g}$ spin-forbidden excitations in the MCD and optical spectra of CrI_3 , which are firmly identified by comparison to Cr L_3 -edge RIXS and CTM calculations. We showed that such excitations are robust to the monolayer limit and revealed a significant field tunability of their MCD response with the magnetic state in AFM few-layer CrI_3 . We associate

the optical brightness of these transitions and their modification with magnetic state to the effects of metal-ligand covalency, as supported by our CTM analysis. These results not only clarify the magneto-optical response of the chromium trihalides, but also provide significant new insight into the role of covalency for the mechanisms of field-tunable magneto-optical properties and the brightening of spin-forbidden multiplet excitations in correlated insulators.

Note added.—Recently, we became aware of another RIXS study of CrI_3 [100].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [101].

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