

Ferromagnetism and Spin-Polarized Luminescence in Lead-Free CsEuCl₃ Perovskite Nanocrystals and Thin Films

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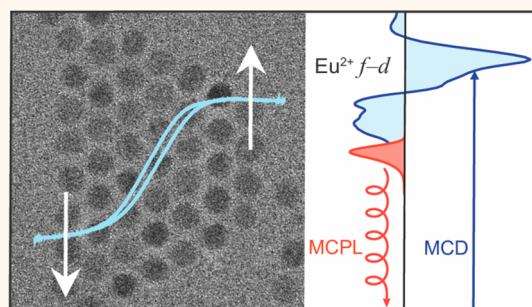
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ABSTRACT: The emergence of next-generation spintronic and spin-photonic technologies will be aided by the development of materials showing strongly coupled magnetic, electronic, and optical properties. Through a combination of magneto-photoluminescence and magnetic circular dichroism spectroscopies we demonstrate strong magneto-optical responses from CsEuCl₃ perovskite nanocrystals and thin films in the near-UV/visible region, stemming from the *f*–*d* transitions centered at the B-site Eu²⁺ cations. We show that this material undergoes a ferromagnetic phase transition at ~3 K in both the nanocrystal and thin-film samples, resulting in complete spin alignment and indicating intrinsic ferromagnetism. We also report the observation of spin-polarized photoluminescence in the presence of a magnetic field at cryogenic temperatures, saturating with a large polarization ratio ($\Delta I/I = (I_L - I_R)/(I_L + I_R)$) of nearly 30% at modest magnetic fields (~2 T). These results highlight CsEuCl₃ as an intrinsically ferromagnetic, luminescent metal-halide perovskite with potentially interesting implications for future spin-based technologies using perovskites.

KEYWORDS: ferromagnetism, spin-polarized luminescence, perovskite, magneto-optical spectroscopy, magnetic circular dichroism spectroscopy



Ferromagnetic EuE (E = O, S, Se, Te) semiconductors have long been employed for demonstration of spintronic functionality in transport measurements.¹ These materials have been prepared across a range of morphologies, including both bulk and nanocrystalline forms.^{1–3} Despite the strong oscillator strength of the Eu²⁺ *f*–*d* transition that defines their band gaps, these materials show weak photoluminescence (PL) in the bulk^{4,5} and little or no intrinsic PL in nanocrystals. Materials that combine luminescence with ferromagnetism provide an additional magneto-optical degree of freedom that could prove attractive for basic research toward next-generation spin-photonic technologies. Recently, metal-halide perovskites have received pronounced attention due to their high PL quantum yields,^{6,7} tunable band gaps,^{8,9} and large absorption coefficients.^{10,11} Despite several studies of the spin properties of nonmagnetic lead-halide perovskites,^{12–14} magnetic perovskites remain underdeveloped. Previous reports of magnetic perovskites have relied on open-shell dopants such as Mn²⁺ or Fe³⁺ to impart magnetic functionality. In some cases, ferromagnetic ordering is observed but with small magnetic moments that indicate its origin in ferromagnetic domains or inclusions, with the majority of the dopant population remaining para-

magnetic.^{15–18} Some observations have demonstrated weak coupling between such magnetism and the optical properties of the materials.¹⁹ Further advances in the development of magnetic metal-halide perovskites will generate attractive opportunities to access spin-controlled electronic and photonic properties, or photon-controlled spin properties, in this versatile class of materials.

Here, we report on the magneto-optical properties of the perovskite CsEuCl₃ prepared in both nanocrystalline and bulk (thin-film) morphologies. Although the nanocrystal synthesis of this material has been recently reported,²⁰ the magnetic or magneto-optical properties of these nanocrystals have not yet been reported. Even in the bulk literature there are very few studies of CsEuCl₃,^{21,22} and none that have addressed its magnetism or magneto-optical properties. Using magnetic

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circular dichroism (MCD) spectroscopy, we now show that CsEuCl₃ displays a very strong magneto-optical response in the near-UV/visible region associated with its Eu²⁺ *f*–*d* optical band gap. Moreover, we identify a magnetic phase transition to a ferromagnetic phase showing a sizable magnetic hysteresis below ~3 K. We also report variable-temperature PL measurements, demonstrating strongly enhanced luminescence at low temperatures. Magneto-PL measurements further demonstrate the emission of circularly polarized light with a polarization ratio of nearly 30% at relatively small magnetic fields. The magneto-optical responses of CsEuCl₃ greatly exceed those reported for any other metal-halide perovskites to date. These distinctive magnetic and magneto-optical properties in CsEuCl₃, in conjunction with its perovskite structure and its accessibility through both chemical and vapor-deposition routes, may have promising ramifications for future spin-based technologies built around metal-halide perovskites.

RESULTS AND DISCUSSION

Colloidal CsEuCl₃ nanocrystals were prepared following literature procedures (see Methods).²⁰ Figures 1a,b show

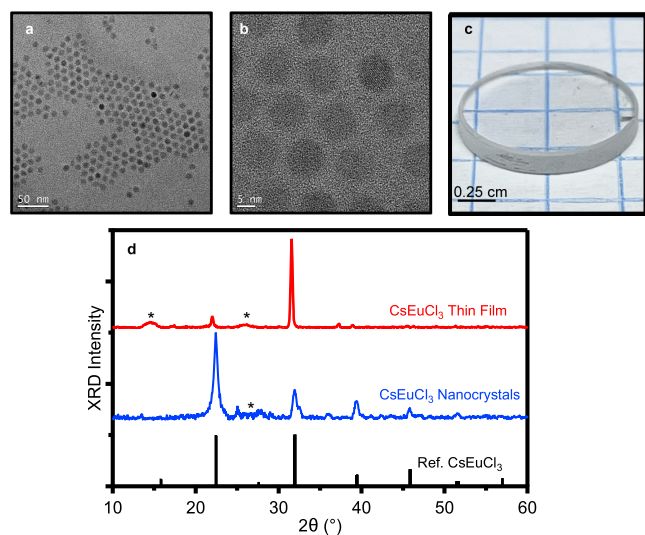


Figure 1. (a,b) TEM images of CsEuCl₃ nanocrystals. (c) Photograph of the thermally evaporated CsEuCl₃ thin film. (d) Powder X-ray diffraction patterns of CsEuCl₃ nanocrystals and CsEuCl₃ thin film compared to a CsEuCl₃ reference pattern (tetragonal, ICSD Coll. Code 201316). The asterisks correspond to additional scattering peaks due to the Kapton tape used for air-free encapsulation.

TEM images of the CsEuCl₃ nanocrystals studied here. The nanocrystals are spherically shaped and nearly monodisperse, with $d = 10.1 \pm 0.7$ nm. Figure 1c shows a photograph of the thermally evaporated CsEuCl₃ thin film also studied here (see Methods). This film, grown on a quartz substrate, has excellent transparency and shows negligible scattering. The film thickness is estimated to be 80 nm based on quartz crystalline microbalance readings during deposition. Figure 1d plots powder X-ray diffraction data collected for the nanocrystals and thin film. These data show peaks consistent with perovskite CsEuCl₃; the experimental data are referenced against the tetragonal phase, but it is not possible to distinguish between cubic (*Pm*-3*m*, $a = b = c = 5.62$ Å, ICSD Coll. Code 31463)²¹ and tetragonal (*P4mm*, $a = b = 5.59$ Å, $c = 5.62$ Å,

ICSD Coll. Code 201316)²² structures from these data. A similar structural ambiguity was also encountered in the analogous lead-halide perovskites.²³ The peak intensity ratios in the thin-film data indicate preferential growth along the [200] direction. We also note the presence of a weak shoulder on the [200] diffraction peak in the nanocrystal data that is not present in the thin-film XRD data. The peaks are not sufficiently resolved to definitively identify this shoulder, but it could conceivably come from an impurity that is not removed by our sample purification steps. The CsEuCl₃ nanocrystals and thin films are unstable in air due to facile oxidation of Eu²⁺ to Eu³⁺,²⁰ and the asterisks in Figure 1d denote additional features that arise from the encapsulating Kapton tape used for the air-free X-ray diffraction measurements (see Methods).

Figure 2a plots room-temperature absorption, PL, and PLE spectra collected for the CsEuCl₃ nanocrystals. The absorption spectrum shows an intense band with pronounced structure centered around 3.7 eV. At higher energies, the main absorption feature decreases in intensity and a second, deep-UV feature displays a gradual onset. The main PL feature is centered around 2.88 eV (430 nm), close to the absorption onset. A second, less-intense PL feature is observed at ~2.2 eV, with large batch-to-batch variations in its intensity. The PLE spectra of both PL features follow the nanocrystal absorption spectrum well. The low-energy PL does not increase in intensity when the nanocrystals are exposed to air (see Supporting Information (SI) Figure S1), ruling out the possibility that it arises from aerobic degradation of the CsEuCl₃. Moreover, the PLE data (Figure 2a) show that this second PL peak is sensitized by CsEuCl₃ itself, meaning that the anomalous Eu²⁺ is intimately connected to the CsEuCl₃ lattice. Collectively, the data point to this second PL feature arising from additional Eu²⁺ species within the CsEuCl₃ lattice, for example, associated with point defects, rather than from lattice decomposition products.

Figure 2b shows variable-temperature PL spectra collected from these CsEuCl₃ nanocrystals. The PL intensity decreases with increasing temperature but its energy is temperature-independent, contrary to what would be expected for an excitonic transition. Instead, the data in Figures 2a,b are consistent with the spectroscopy of CsEuCl₃ being dominated by localized Eu²⁺ $4f^65d^1 - 4f^7$ transitions. In the octahedral B-site coordination environment of CsEuCl₃, the empty Eu²⁺ *5d* orbitals of the $4f^7(^8S_{7/2})$ ground state are split into *t*_{2g} and *e*_g sets, with the *t*_{2g} set becoming the lowest unoccupied orbitals. The structured absorption band centered at ~3.5 eV thus corresponds to the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_1)5d^1(t_{2g})$ transition, with fine structure arising from spin–orbit splittings within the $4f^65d^1$ excited-state configuration. The growing absorption above ~4.0 eV is attributed to the onset of $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_1)5d^1(e_g)$ transitions.

Figure 2c plots PL decay curves for these CsEuCl₃ nanocrystals collected at a series of temperatures from 15 to 300 K. From these data, the PL decays with a time constant of ~233 ns at 15 K that decreases to ~12 ns at room temperature. In bulk Eu²⁺-doped alkali halides, the Eu²⁺ $4f^65d^1 \rightarrow 4f^7$ lifetime is reported to be temperature independent with a value of ~850 ns, reasonably approximated as the Eu²⁺ radiative lifetime in these lattices.^{24,25} Eu²⁺-doped CsCaCl₃ single crystals also show a PL decay time of ~1 μs at ~45 K,²⁶ but their anomalous temperature dependence makes direct comparison with the CsEuCl₃ PL difficult. Overall, the 15 K

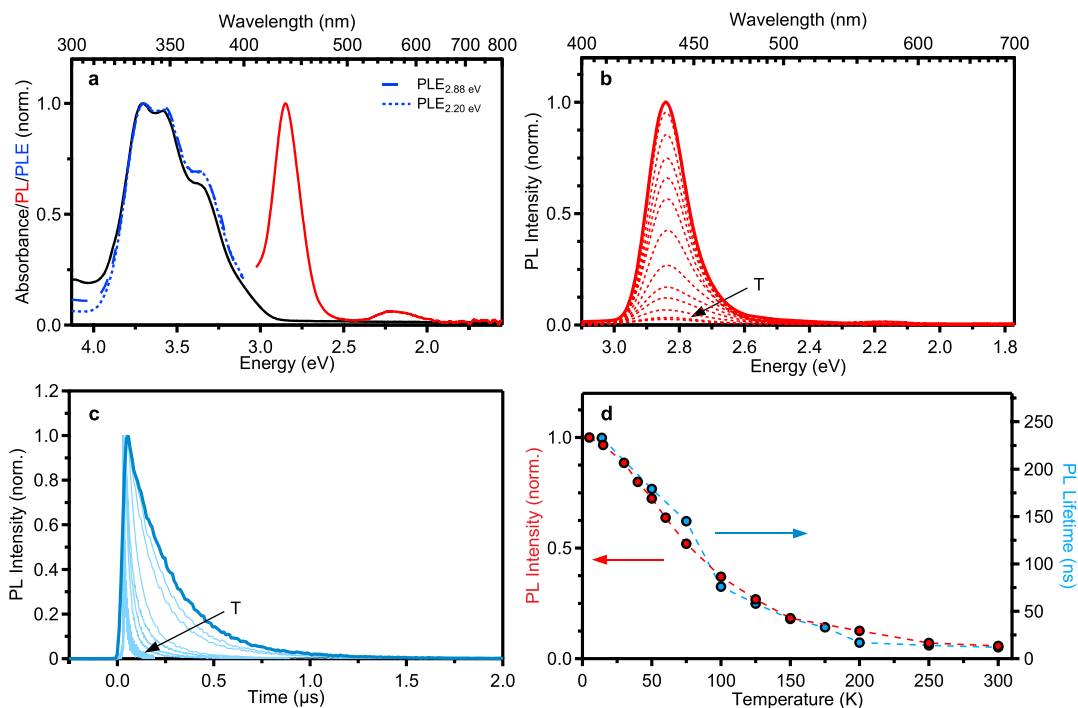


Figure 2. (a) Room-temperature absorption (black), PL (red), and PLE (blue) spectra of colloidal CsEuCl₃ nanocrystals. (b) Variable-temperature PL spectra of CsEuCl₃ nanocrystals collected between 5 and 300 K, excited with 375 nm light. (c) Variable-temperature TRPL spectra of CsEuCl₃ nanocrystals excited with 355 nm laser pulses fired at a repetition rate of 50 Hz, collected between 15 and 300 K. All PL lifetimes were fit with biexponential decay functions. The room-temperature average decay time was 12 ns, and the average decay time increased to 233 ns at 15 K. (d) Scatter plot of integrated PL intensities (red) and average PL lifetimes (blue) plotted as a function of temperature.

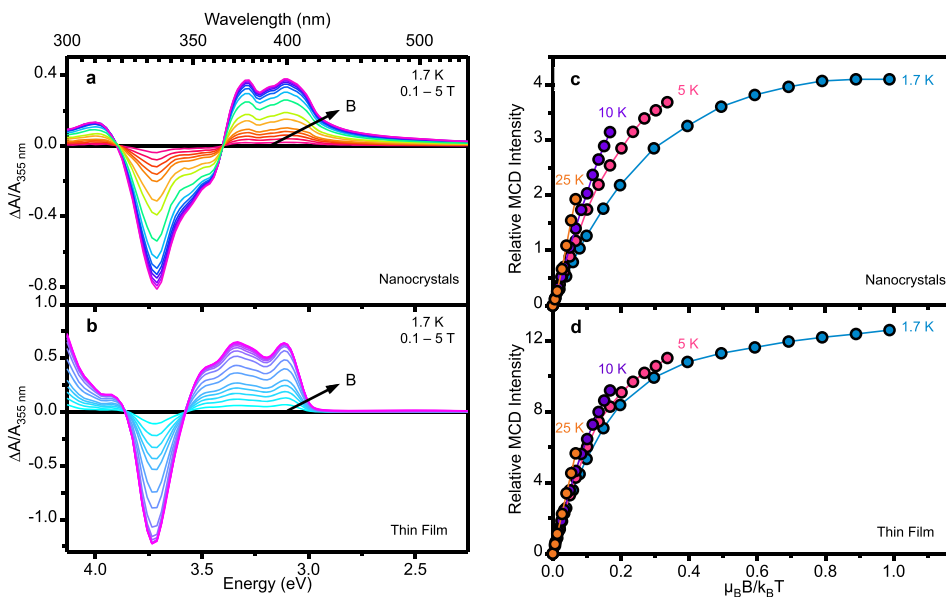


Figure 3. Variable-field MCD spectra of CsEuCl₃ nanocrystals (a) and thin film (b) collected between 0.1 and 5 T at 1.7 K. (c,d) Scatter plots of total integrated MCD intensity vs $\mu_B B/k_B T$. The temperature dependence and saturation at large B/T are consistent with a paramagnetic ground state. The nesting of isotherms indicates a temperature-dependent Boltzmann population distribution over a split ground-state manifold.

nanocrystal PL lifetime of 233 ns observed here is consistent with assignment of this PL as a $\text{Eu}^{2+} 4f^6 5d^1 \rightarrow 4f^7$ transition.

Figure 2d summarizes the variable-temperature PL data from Figures 2b,c and shows that the $4f^6 5d^1 \rightarrow 4f^7$ PL lifetime and intensity both decrease with increasing temperature in the

same manner, indicating the presence of thermally activated nonradiative losses with a very small energy barrier. Indeed, both metrics drop by $\sim 95\%$ over this temperature range, consistent with the low room-temperature PLQY ($\sim 2\%$) reported previously.²⁰ Most likely, this temperature depend-

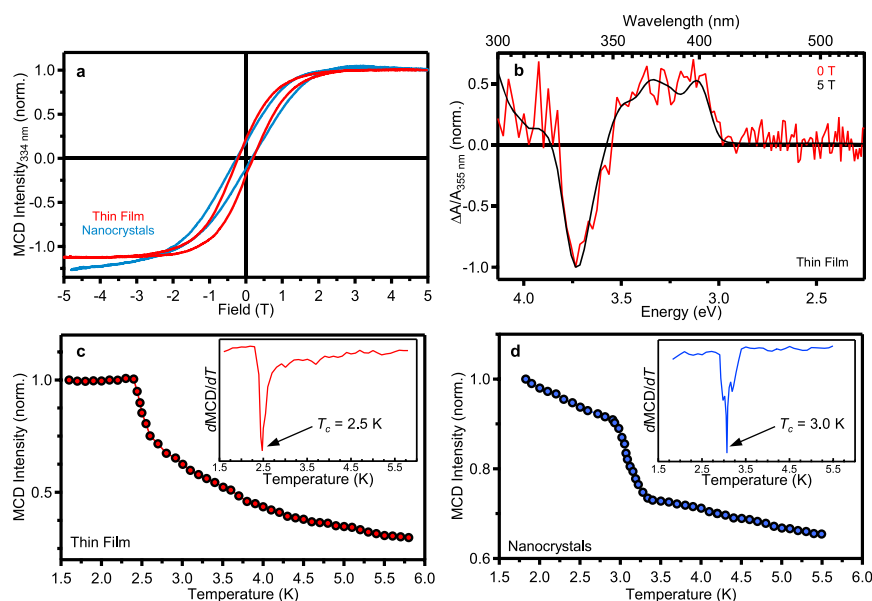


Figure 4. (a) 1.7 K magnetic field-sweep data for CsEuCl₃ nanocrystals and thin film, collected by monitoring the MCD intensity of the feature centered around 3.71 eV (334 nm) as a function of applied magnetic field. (b) 0 T (remanent) MCD spectrum of the CsEuCl₃ thin film collected at 1.7 K following hysteresis measurement, plotted together with the 5 T spectrum of the same sample measured under the same conditions and scaled for comparison. (c,d) Curie temperature plots of the thin film and nanocrystal samples collected at 0.15 T monitoring the MCD intensity centered around 3.71 eV (334 nm) as a function of temperature. The Curie temperatures were found to be ca. 2.5 and 3.0 K for the thin film and nanocrystals, respectively.

ence stems from accelerating intranano-crystal energy migration enabled by thermal broadening of the absorption and emission bands, which increases donor–acceptor spectral overlap. Energy migration commonly leads to nonradiative relaxation in related materials with high concentrations of luminescent centers, because the excitation can sample a large volume during its lifetime and thus has a high probability of finding a trap. Notably, the weaker, low-energy PL from Figure 2a is not observed in the low-temperature PL spectra shown in Figure 2b and appears only above ~200 K (SI Figures S2 and S3), consistent with thermally activated energy migration and trapping. In a previous report, the room-temperature PLQY of CsEuCl₃ nanocrystals was improved from 2 to 6% after a postsynthetic halide surface treatment.²⁰ This modest PLQY enhancement may suggest that at least some nonradiative losses in these nanocrystals can be attributed to surface trapping, but it also suggests the prevalence of internal lattice defects as well. A similar and even broader sub-bandgap PL feature is observed in the CsEuCl₃ thin films as well, but this feature disappears with annealing (see SI), consistent with the relevant trap involving a native defect. In many Eu²⁺-doped halide crystals, Eu²⁺ can occupy multiple lattice sites with different coordination numbers,^{27,28} leading to multiple PL peaks and nonradiative recombination sites; trapping in CsEuCl₃ is thus tentatively attributed to such defects, for example, a combination of Eu_{Cs}, Eu_{Cl}, and Eu_{surface/grain boundary}. Further improvement of this material's PLQY at high temperatures will therefore require suppressing formation of internal lattice defects. Overall, these observations indicate thermally activated energy migration in CsEuCl₃ that results in efficient energy trapping at both nonradiative and emissive defect sites.

Because Eu²⁺ is magnetic, magneto-optical spectroscopies were applied to investigate the transitions seen by absorption and PL in more detail. Figure 3a plots CsEuCl₃ nanocrystal

MCD spectra collected at 1.7 K as a function of magnetic fields between 0.1 and 5.0 T. These spectra show a derivative-shaped MCD band centered around 3.5 eV and an additional positive MCD feature around 4.0 eV, coinciding with the energetic positions of the observed absorption features. The CsEuCl₃ MCD spectrum resembles those of dilute Eu²⁺ dopants in other halide lattices (Eu²⁺:CsCl and Eu²⁺:CsNaEuCl₃,²⁹ see SI Figure S6), consistent with assignment of this electronic transition in CsEuCl₃ as the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(t_{2g})$ transition of Eu²⁺. These data show a trend of increasing MCD intensity with increasing magnetic field. All components of the MCD fine structure gain intensity with increasing field and saturate at the highest fields in a similar manner.

Figure 3b plots parallel data collected for the CsEuCl₃ thin film shown in Figure 1. The thin-film spectra are very similar to the nanocrystal data, with the main differences being narrower features at 3.1 and 3.7 eV and the absence of the low-energy MCD tail observed in the nanocrystal spectra. Due to the much larger surface-to-volume ratios of the nanocrystals, we interpret these spectral differences as reflecting the contributions of surface or near-surface Eu²⁺ ions with slightly different coordination environments to the nanocrystal spectra. Indeed, the additional MCD component present in the nanocrystals (SI Figure S5) is similar to the MCD spectra of Eu(OCN)₂ nanocrystals;³⁰ Eu(OCN)₂ crystallizes in a layered structure, resulting in a Eu²⁺ coordination environment that may be similar to the proposed surface Eu²⁺ ions in CsEuCl₃. Overall, the MCD spectra observed for CsEuCl₃ are characteristic of Eu²⁺ ions in halide crystals and confirm assignment of the dominant CsEuCl₃ nanocrystal absorption band to the f – d transitions of B-site Eu²⁺ ions. Notably, the MCD signal amplitudes in CsEuCl₃ (e.g., $\Delta A/A_{\text{max}} \sim 1.2$, Figure 3b) are a factor of ~20× larger than those of CsPbBr₃ ($\Delta A/A_{\text{max}} \sim 0.06$, unpublished results) under similar measurement conditions and even a factor of ~2× larger than those of Mn²⁺:CdSe

quantum dots showing giant excitonic Zeeman splittings,³¹ highlighting the very large magneto-optical response of CsEuCl₃.

The CsEuCl₃ MCD intensities decrease with increasing temperature (SI Figure S7), consistent with our assignment of this as C-term MCD intensity³² reliant upon magnetization of the Eu²⁺ ground state. The full variable-temperature, variable-field MCD data sets for these two CsEuCl₃ samples are summarized in Figure 3c,d, plotted as MCD isotherms ($I(B)_T$ vs $\mu_B B/kT$). The 1.7 K isotherms in Figure 3c,d both approach saturation at large B/T , consistent with a dominant C-term contribution. Further, the isotherms for different temperatures do not all lie on top of one another as for a simple paramagnet but instead show nesting indicative of a more complicated magnetic ground state. Often, such nesting reflects splittings of magnetic ground states through either first- or second-order spin–orbit interactions, the latter coupled with low-symmetry distortions, but the ⁸S_{7/2} ground state of Eu²⁺ has no first-order orbital angular momentum and its valence *f*-shell electrons are only weakly influenced by low-symmetry crystal fields. Indeed, the crystal-field splitting of the Eu²⁺ ground state is typically smaller than $k_B T$ across all temperatures²⁹ and is therefore not responsible for this nesting.

To probe the magnetic ground state further, field-sweep MCD measurements were performed at the lowest temperature achievable in our MCD instrument, ~ 1.7 K. Figure 4a plots the normalized MCD intensities of the strong negative feature centered around 3.71 eV (334 nm) for both the nanocrystal and thin-film samples, measured during continuous “positive” and “negative” magnetic-field sweeps at 1.7 K. The data for both samples reveal clear magnetic hystereses characterized by a remanence of $\sim 12\%$ and a coercivity of 0.2 T. Figure 4b shows that the MCD spectrum measured at 0 T (remanence) is superimposable upon the high-field (5 T) MCD spectrum of the same sample, indicating that this remanent magnetization is associated with CsEuCl₃ itself rather than with impurities or other spurious sources. The saturation observed at high fields, particularly cleanly in the thin film, demonstrates that all Eu²⁺ participate in this magnetic ordering, and not just a small subset of Eu²⁺ ions. The nanocrystals may require larger fields to achieve full saturation because of contributions from surface Eu²⁺ that are poorly integrated into the ferromagnetic ordering. This interpretation is supported by variable-temperature measurements. Figures 4c,d plot the normalized 0.15 T MCD intensities of the same 3.17 eV feature for the thin film and nanocrystals as a function of temperature. These data show distinct discontinuities in the magnetization, attributable to the ferromagnetic phase transition. The insets in Figures 4c,d plot $d\text{MCD}/dT$, from which Curie temperatures of $T_C \sim 2.5$ and 3.0 K are obtained for the thin film and nanocrystals, respectively. Whereas the thin-film magnetization plateaus below the ordering temperature, the nanocrystal magnetization continues to rise slightly, supporting the interpretation above that surface Eu²⁺ contributes a paramagnetic signal on top of the nanocrystal ferromagnetism in the latter.

The rich magnetism of CsEuCl₃ demonstrated above should also manifest itself in the PL of these materials. Figure 5 plots circularly resolved PL spectra of the CsEuCl₃ nanocrystals measured at 1.7 K in applied magnetic fields of 0–5 T. The data show a large disparity between left- and right-circularly polarized PL intensities in an applied magnetic field. The inset plots the PL polarization ratio, $\Delta I/I = (I_L - I_R)/(I_L + I_R)$.

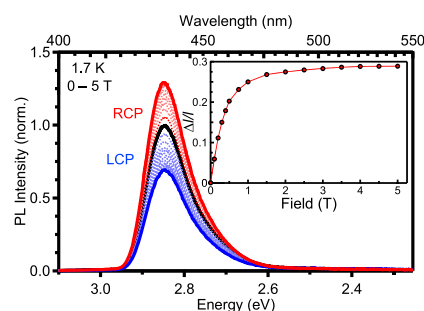


Figure 5. CsEuCl₃ nanocrystal MCPL spectra collected at 1.7 K between 0 and 5 T. Inset: Scatter plot of nanocrystal MCPL polarization ratio ($\Delta I/I$) vs magnetic field at 1.7 K.

These data show a rapidly increasing degree of circular polarization with increasing magnetic field, saturating at $\Delta I/I \sim 0.29$, indicating strongly spin-polarized PL from perovskite CsEuCl₃ nanocrystals. For comparison, $\Delta I/I$ is ~ 0.05 for MAPbI₃ thin films under similar measurement conditions.³³ We note that $\Delta I/I$ in CsEuCl₃ reaches saturation at a lower field than needed to saturate the MCD intensity at the same temperature (SI Figure S10); the MCPL field dependence reflects the magnetization (and potentially also spin-relaxation dynamics) of the emissive excited state rather than magnetization of the ground state.

Characterization of the CsEuCl₃ electronic structure, as informed by the optical and magneto-optical spectroscopies described above, is fundamentally important for assessing the potential of this material for future spin-based applications. Using MCD and PL spectroscopies, we show here that the strong first absorption band of CsEuCl₃ is a Eu²⁺ *f*–*d* transition, similar to EuE (E = O, S, Se, Te) ferromagnetic semiconductors.² This assignment defines the nature of the optical gap in CsEuCl₃. The data reported here suggest that this transition is fairly isolated, similar to the *f*–*d* transitions of Eu²⁺ ions diluted into other chloride lattices. This result is consistent with the absence of confinement effects in the energy of this transition upon changing from thin-film to nanocrystal morphologies. The primary difference observed between the CsEuCl₃ nanocrystals and thin films is that the nanocrystals show additional spectral and magnetic contributions relative to the thin films, attributed to surface Eu²⁺.

The magnetic properties reported here for CsEuCl₃ are not found in any other metal-halide perovskites. Ferromagnetic ordering of Eu²⁺ spins is observed with $T_C = 2.5$ – 3.0 K. The similar magnetic hystereses and ordering temperatures in nanocrystals and thin films indicate that this ferromagnetism is intrinsic to bulk CsEuCl₃. Importantly, all Eu²⁺ participate in this ferromagnetic ordering, contrasting CsEuCl₃ with the several magnetically doped metal-halide perovskite and related semiconductors recently reported to show ferromagnetism;^{15–18} in the latter, the magnetic ions are present at relatively low concentrations (compared to CsEuCl₃) and only minority populations appear to order ferromagnetically. Those materials are thus arguably better described as metal-halide perovskites containing ferromagnetic inclusions or domains, whereas CsEuCl₃ is a *bona fide* ferromagnetic metal-halide perovskite. We note that another class of 2D hybrid metal-halides has also shown ferromagnetism in some compositions, e.g., (RNH₂)₂MCl₄ (M = Cr, Cu; R = alkyl),^{34,35} but these bear little resemblance to the perovskite structure.³⁶

The excited-state localization observed spectroscopically implies that this ferromagnetism results from Eu^{2+} - Eu^{3+} f - d exchange and superexchange, as in the canonical EuE magnetic semiconductors.¹ For comparison, ferromagnetism has also been reported in EuCl_2 and EuI_2 ($T_C = 1.6$ – 1.8 K; 9- and 7-coordinate, respectively), but it is absent in EuBr_2 (8-coordinate) and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{EuI}_4$ down to 1.1 and 1.8 K, respectively.^{37,38} Much more stable ferromagnetism is observed in the EuE lattices ($\text{E} = \text{O}, \text{S}, \text{Se}$; $T_C = 70, 16, 6$ K, respectively).^{39,40} Although MCD spectroscopy does not show the same large d -band spin splittings in CsEuCl_3 as found in, for example, EuS nanocrystals,⁴¹ the observation of ferromagnetic ordering in a metal-halide perovskite may motivate studies targeting integration of magnetism into existing or future perovskite technologies. For example, the strong spin-polarizable PL found in CsEuCl_3 introduces an attractive functionality for potential spin-photonics applications not found in other perovskites. Moreover, CsEuCl_3 shares the same lattice structure and similar lattice parameters with other popular metal-halide perovskites based on Pb^{2+} and Sn^{2+} , and it may therefore be possible to grow architectures interfacing ferromagnetic CsEuCl_3 with commensurate metal-halide perovskites such as CsPbCl_3 or CsSnCl_3 that possess complementary functionalities, thereby expanding the possibilities for manipulating the optoelectronic properties of perovskites. Heterointerfacing of this type may also be accessible on the nanoscale using wet-chemical methods.

CONCLUSION

Spectroscopic results are presented that elucidate the fundamental electronic structure of CsEuCl_3 , both in nanocrystals and in bulk form. PL in this material is assigned to the f - d optical transition of Eu^{2+} in the B site of the perovskite CsEuCl_3 lattice, and the corresponding f - d absorption band defines the optical gap of the material. The absorption, MCD, and PL data all indicate that this transition is fairly localized. Variable-temperature PL measurements suggest efficient energy migration within photoexcited CsEuCl_3 that accelerates with increasing temperature and that leads to trapping and nonradiative relaxation. In the nanocrystals, for example, the PL intensity decreases by a factor of ~ 20 between 5 K and room temperature. MCD spectroscopy also reveals ferromagnetic ordering with $T_C = 2.5$ – 3.0 K in CsEuCl_3 , and magneto-PL demonstrates spin-polarizable emission with maximum polarization ratios of $\sim 30\%$. This strong ferromagnetism combined with the strong low-temperature PL and the large coupling between the magnetism and the electronic transitions of CsEuCl_3 distinguish this material among metal-halide perovskites. When combined with the scalability of thermal evaporation methods for large-area thin-film growth and the processability of colloidal nanocrystals, these results present CsEuCl_3 as an attractive and flexible candidate for integration of magnetism into future spintronic or spin-photonics architectures based on metal-halide perovskites.

METHODS

Chemicals. Unless otherwise stated, all chemicals were used as purchased without further purification. Nanocrystal syntheses employed Cs_2CO_3 (99% Alpha Aesar), EuCl_3 (99.99%, Sigma-Aldrich), 1-octadecene (ODE, 90% Sigma-Aldrich), oleylamine (OAm, 70% Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), and trioctylphosphine (TOP, 97% Sigma-Aldrich). Thin films were

prepared with EuCl_2 (99.99%, Sigma-Aldrich) and CsCl (99.999%, Strem).

Preparation of Eu^{2+} precursor. One mmol of EuCl_3 was added to 5 mL of OAm and evacuated at 120°C for 60 min. The solution was then reacted at 300°C under N_2 for 40 min, upon which it was left to cool to room temperature and transferred to a glovebox for future use.

Preparation of Cs-Oleate. 0.2 g Cs_2CO_3 was added to 7.5 mL ODE and 0.7 mL OA. The solution was evacuated at 120°C for 60 min, or until all residual carbonic acid was removed. The flask was then switched to N_2 and heated to 150°C for 30 min.

Preparation of CsEuCl_3 nanocrystals. The CsEuCl_3 nanocrystal synthesis was adapted from a previous literature report.²⁰ In a standard reaction, 5 mL ODE, 0.5 mL TOP, and 0.25 mL OA were degassed at 120°C for 60 min, upon which the reaction flask was switched to N_2 and 2 mL of the Eu^{2+} -precursor was added. The temperature was raised to 250°C and held for 25 min. Then, 2 mL of Cs-oleate was added to the Eu^{2+} flask and the reaction proceeded for 45 min after the temperature restabilized at 250°C . The reaction was quenched with a room-temperature water bath, and 6 mL of hexanes was added. The product was separated from the reaction solution by centrifuging at 8000 rpm for 5 min, followed by resuspension of the pellet in hexane, and repeated once. After the second resuspension in hexane, the nanocrystals were purified via further centrifugation at 4000 rpm for 1 min, where the supernatant was collected and finally centrifuged at 2000 rpm for 2 min. The suspended nanocrystalline product was then collected. CsEuCl_3 decomposes in air, so all sample synthesis, handling, transport, and measurement was performed with careful exclusion of air.

Preparation of Thin Films. Thin-film samples were prepared on quartz substrates via thermal evaporation. In a standard CsEuCl_3 deposition, EuCl_2 and CsCl were simultaneously evaporated in stoichiometric amounts at a rate of $\sim 0.25 \text{ \AA/s}$, as monitored by quartz crystal microbalances. After deposition, the film was annealed at 300°C for 30 min under inert atmosphere. Eu^{2+} -doped CsCl thin films were prepared by simultaneous thermal evaporation of EuCl_2 and CsCl with no postdeposition annealing. CsEuCl_3 decomposes in air, so all sample synthesis, handling, transport, and measurement was performed with careful exclusion of air.

Analytical Characterization. Thin-film and nanocrystal samples were encapsulated in Kapton tape under inert conditions prior to collecting X-ray diffraction data. X-ray diffraction measurements were performed using a Bruker D8 Discover Microfocus diffractometer with a $\text{Cu K}\alpha$ source ($1.54 \text{ \AA}$). Transmission electron microscope images were collected using a Technai G2 F20 Supertwin TEM operating at 200 kV.

Electronic Absorption, PL, Time-Resolved PL Spectroscopies. Electronic absorption spectra were collected at room temperature using Cary 60 and Cary 5000 spectrometers. Variable-temperature photoluminescence (PL) and time-resolved photoluminescence (TRPL) data were collected by sandwiching drop cast nanocrystals between two quartz disks and loading into a closed-cycle helium cryostat. Continuous-wave PL spectra were collected by exciting the sample with a 375 nm diode laser and detected on a liquid-nitrogen-cooled CCD mounted on a monochromator. Time-resolved PL data were collected by irradiating the sample with 355 nm light generated from the third harmonic of an Ekspla Nd:YAG laser firing at a repetition rate of 50 Hz, with the PL detected by a Hamamatsu R928 photomultiplier tube mounted on a monochromator. PL excitation (PLE) measurements as well as some thin-film PL measurements were performed using an Edinburgh FLS1000 fluorometer equipped with a xenon flash lamp and visible PMT detector. PLE measurements were performed by monitoring the PL intensity at the desired wavelength while tuning the excitation wavelength, and PL measurements on this instrument were performed using 375 nm excitation.

Magnetic Circular Dichroism (MCD), Magnetic Circularly Polarized Luminescence (MCPL) Spectroscopies. Nanocrystal samples for magneto-optical measurements were prepared as a mull suspension by mixing dried nanocrystals with polydimethylsiloxane,

then sandwiched between two quartz disks. Thin film samples were prepared by thermally depositing directly onto a quartz disk. Magneto-optical data were collected by loading samples into a superconducting magneto-optical cryostat equipped with a variable-temperature sample compartment (Cryo-Industries SMC-1659 OVT) oriented in the Faraday configuration. MCD spectra were collected using an Aviv 40DS spectropolarimeter. MCPL spectra were collected using 375 nm laser diode excitation. The sample PL was guided along the magnetic field axis through a liquid crystal variable retardation plate set to $\lambda/4$ at the emission maximum, followed by a linear polarizer to separate left- and right-circularly polarized components. The PL was then passed through a fiber-optic cable and detected on a liquid nitrogen-cooled CCD mounted on a monochromator. MCPL ratios are defined as $\Delta I/I = (I_L - I_R)/(I_L + I_R)$ following sign conventions outlined in Piepho and Schatz.³² At liquid helium temperatures all sample depolarization ratios were checked by matching the CD signal of a chiral molecule placed before and after the sample along the optical path. The depolarization ratios of all samples were $\sim 5\%$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.1c09257>.

Additional spectra from the variable-temperature PL measurements, additional temperature- and field-dependent MCD spectra and scatter plots, as well as thin film characterization (PDF)

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Notes

The authors declare no competing financial interest.

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