Rare-earth (RE) nanolaminates Mo$_4$RE$_4$Al$_7$C$_3$ featuring ferromagnetism and mixed-valence states

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Rare-earth-based (RE) nanolaminates have attracted attention recently because of their complicated magnetism and their potential as precursors for strongly correlated two-dimensional materials. In this work, we synthesized a class of nanolaminates with a Mo$_4$RE$_4$Al$_7$C$_3$ chemistry, where RE = Ce or Pr. Powder samples of both phases were characterized with respect to structure and composition. Single crystals of Mo$_4$Ce$_4$Al$_7$C$_3$ were used for magnetization measurements. The crystal structure was investigated by means of x-ray diffraction and scanning transmission electron microscopy. Magnetization analysis reveals a ferromagnetic ground state with a Curie temperature of $\sim$10.5 K. X-ray absorption near-edge structure provides experimental evidence that Ce is in a mixed-valence state. X-ray magnetic circular dichroism shows that only the Ce atoms with 4$d^1$ configuration occupying one of the two possible sites are ferromagnetically coupled, with a saturation moment of $\sim$1.2 $\mu_B$ per atom. We thus classify Mo$_4$Ce$_4$Al$_7$C$_3$ as a ferromagnetic, mixed-valence compound.

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I. INTRODUCTION

Rare-earth (RE) compounds exhibit a variety of magnetic and electronic ground states through the hybridization between 4$f$ and conduction electrons [1–3]. Heavy fermion compounds, primarily those containing Ce and Yb, are prototype systems for the study of quantum critical [4] and collective quantum states [5]. In addition to the orbital and valence degrees of freedom generating a multitude of ground states [6], the discovery of new layered RE compounds that can act as precursors for the synthesis of two-dimensional (2D) magnetic materials is another fruitful avenue. In the latter domain, it has recently been shown that RE intercalation in graphene grown on Si-face SiC substrates can lead to substantial doping of the graphene layers and quite high 2D electron densities [7]. However, transferring large-scale and mono- or multilayers while preserving the integrity of the RE dopants and maintaining regular order constitutes a real challenge. An alternative strategy is to use 2D systems, for which high metallic carrier densities are an intrinsic material property, and to incorporate the RE element as a regular, ordered member of the original lattice in order to optimize compound stability and robustness. A first step toward this goal is to synthesize three dimensional (3D) layered compounds, which can be exfoliated to form magnetic 2D systems, in which the RE’s magnetism is potentially transferred to the itinerant electrons and used for electron spin control and/or injection. Before proceeding further, we note that in 2011 it was shown that it is relatively straightforward to selectively etch individual atomic layers (mostly Al) from the laminated ternary 3D carbides (MAX phases; see below) for conversion into their 2D metal carbide (MXene) counterparts [8].

In the present paper, we report on the synthesis of a family of magnetically ordered nanolaminates with a Mo$_4$RE$_4$Al$_7$C$_3$ chemistry. This discovery was made while exploring the so-called i-MAX phases. The $M_{n+1}AX_n$ (MAX) phases, where M is an early transition metal, A is an A-group element (mostly groups 13 and 14), X is C and/or N, and $n = 1 − 3$, are machinable metallic carbides/nitrides with a nanomellar structure [9]. In 2017, in-plane ordered or i-MAX phases were reported [10,11]. In these quaternary compounds where $n = 1$, viz. (M$^{I}_{1/3}$, M$^{II}_{2/3}$)$_2$AlC, the M$^{I}$ and M$^{II}$ transition metals are ordered in the M basal plane. When the latter are etched they form i-MXenes [10,12]. The unique feature of the i-MAX phases is the possibility to derive i-MXenes with ordered vacancies or M element order, from the same parent material, through etching of both Al and M$^{II}$ or Al only, respectively [13]. The first i-MAX phase discovered was (Mo$_{2/3}$, Sc$_{1/3}$)$_2$AlC [10]. The fact that Sc could be incorporated in an i-MAX phase led us to try other RE elements. Indeed, we recently synthesized 11 new RE i-MAX phases (Ref. [14]).

During the synthesis of the aforementioned RE i-MAX phases, we discovered a family of RE-based nanolaminates with a chemical formula of Mo$_4$RE$_4$Al$_7$C$_3$—henceforth referred to as the 4473 phases—where RE = Ce or Pr. These phases, though of a different composition compared to the i-MAX phases, display the same characteristic in-plane chem-
ical order of the Mo and RE elements. Not only did we synthesize these materials in powder form, but we also grew relatively large single crystals that, in turn, allowed us to carry out a comprehensive materials characterization, more focused on Mo₄Ce₄Al₇C₃. Calculated Raman-active vibrational modes for this phase were found to be in very good agreement with the measured Raman spectra. Based on magnetization measurements, x-ray absorption near-edge structure (XANES), and x-ray magnetic circular dichroism (XMCD), we find a ferromagnetic response and that at least one of the two inequivalent Ce atomic sites is in a mixed valence state.

II. EXPERIMENT

A. Materials synthesis

1. Powder sample preparation

Powder samples were synthesized at Linköping University (LiU). The starting powders were graphite (99.999%), Mo (99.99%) (Sigma-Aldrich), Al (99.8% Alfa Aesar), Ce (99.9%), and Pr (99.9%) (Stanford Advanced Material). Stoichiometric amounts of the elements were mixed in an agate mortar, heated to 1500 °C in an alumina crucible under flowing argon, and held at that temperature for 5 h. After furnace cooling down to room temperature, the slightly sintered body was crushed manually to obtain fine powders for x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM).

2. Single-crystal growth

Single-crystalline platelets of Mo₄Ce₄Al₇C₃—with areas up to a few mm²—were grown at the LMGP in Grenoble using a high-temperature solution growth process that is quite similar to that already described in Refs. [15,16] for growing MAX phase single crystals. In short, Mo, Ce, and Al are melted in a sealed graphite crucible at 1800 °C in an induction-heated reactor. A soak time of a few hours is used to allow the Mo to melt and the C—from the crucible walls—to dissolve in the melt solution. After soaking, the temperature is reduced to 1500 °C in 0.5 h, and a linear cooling ramp of a few days, down to 800 °C, is used to nucleate and grow the crystals near the molten flux surface that is the coolest point.

Since only the binary phase diagrams are known for the present materials system, the solution composition was chosen by systematically avoiding compositions lying close to any of the existing stable binary compounds. A starting favorable, and typical, Mo:Ce:Al atomic composition is 0.1:0.45:0.45. The crystals are separated from the solidified flux by simply placing the latter for one to two days in a fume hood at room temperature (RT). The oxidation of the excess RE transforms the flux into a yellow powder, leaving behind flux-free single crystals. Due to the structure anisotropy and the lack of screw dislocations, the silver-colored shiny platelets exhibit high aspect ratios. The largest platelet areas were around 3 mm². The average crystals were ≈100 μm thick. Atomic force microscopy images (not shown) suggest that the growth proceeds through a step flow mechanism resulting in regular terraces separated by steps with a height that is, most of the time, equal to one unit cell.

B. Materials characterization and computational details

1. X-ray diffraction

XRD (θ-2θ scans) on the powder samples were performed using a PANalytical X’Pert powder diffractometer, with a Cu source (λ = 1.54 Å). The optics utilized for these measurements were a graded Bragg-Brentano HD with ½° divergent and ½° anticollimating slits for the incident beam side, and a 5 mm anticollimating slit together with a Soller slit for the diffracted beam side. A 5°–90° continuous scan was performed on the sample using a step size of 0.016° with a 10 s time per step.

A metallic Mo₄Ce₄Al₇C₃ single-crystal approximately 0.029 × 0.174 × 0.335 mm³ in size was used at Institut de Chimie de Clermont-Ferrand (ICCF) for the measurement of x-ray intensity data for structural determination on a Bruker APEX2 SC-diffractometer (Appendix A). Determination of the final cell constants is based upon the refinement of the XYZ-centroids of reflections above 20 o (J). Data were corrected for absorption effects using the Numerical Mu formula method (SADABS). The structure was solved and refined at ICCF using the Bruker SHELXTL Software Package [17]. A total of five different single crystals were examined, and all gave the same structure.

2. Scanning transmission electron microscopy

STEM combined with high-angle annular dark-field imaging and selected area electron diffraction (SAED) were performed in the double-corrected Linköping FEI Titan 60–300 operated at 300 kV. The specimens, both powder and single-crystal were prepared by embedding ground powder in a Cu grid with carbon film.

3. Vibrational properties: Raman scattering and computational details

Single-crystal Raman spectra were recorded at LMGP using a HoribaJobin Yvon LabRam spectrometer equipped with a liquid-nitrogen-cooled charge-coupled device detector. The measurements were carried out in the micro-Raman mode at RT. The 514.5 nm exciting line of an Ar⁺ laser was focused to a spot size of ~1 μm on the sample surface with an incident power of 0.7 mW. Raman spectra were calibrated using a silicon reference spectrum.

The vibrational properties of Mo₄Ce₄Al₇C₃ were calculated using the ABINIT package [18], which is based on plane-wave basis sets to represent the electronic wave functions and charge densities. Ab initio calculations were performed using the generalized-gradient approximation (GGA) for the exchange-correlation functional as proposed by Perdew, Burke, and Ernzerhof (PBE) [19]. Optimized norm-conserving Vanderbilt pseudopotentials (ONCVPSP-PBE) [20] were used to describe core-valence interaction. Configurations of C—2s²2p², Al—3s²3p¹, Mo—4s²4p⁶4d¹⁰5s¹, and Ce—5s²5p⁶5d³6s² were treated as valence electrons, and the compound was treated as nonmagnetic (no magnetic moments were included in the calculations). A plane-wave basis set, with a converged energy cutoff 80 Ry, was used to represent the wave functions. The first Brillouin zone was sampled with a 12 × 12 × 12 Monkhorst-Pack k-point grid. Starting with the experimental lattice parameters, the atomic positions
were fully optimized until the largest force was smaller than $2.5 \times 10^{-4} \text{eV/Å}$.

4. Magnetization measurements

We used a commercial Quantum Design MPMS magnetometer for measurements in magnetic fields, $H$, up to 9 T. Quantitative magnetization measurements were performed on a 0.36 mg single crystal in the 2–300 K temperature range. Temperature ramps were achieved both in the field-cooled (FC) and zero-field-cooled (ZFC) modes. Isothermal magnetization curves $M(H)$ were measured up to 300 K. In the paramagnetic regime, the inverse of the magnetic susceptibility was deduced from Arrott-type plots, viz. plots of $M^2$ versus $H/M$.

5. X-ray absorption near-edge structure and x-ray magnetic circular dichroism

X-ray absorption near-edge structure (XANES) and x-ray magnetic circular dichroism (XMCD) spectra, at the Ce $L_{3,2}$ and Mo $L_{3,2}$ edges, were made at the European Synchrotron Radiation Facility (ESRF) beamline ID12 [21]. The source of the x rays was a helical undulator either of Apple-II type for the Ce $L$ edges or HELIOS-II type for the Mo $L$ edges. The XANES spectra were recorded on a mm-sized single crystal using the total fluorescence yield detection mode. For the XMCD measurements, a magnetic field of 1 T was applied collinear to the incoming x-ray beam and perpendicular to the sample surface, i.e., along the $c$ axis. The XMCD signal was obtained as a direct difference of the XANES spectra recorded with right and left circularly polarized x rays. The sample was cooled down to 2.1 K. To ensure that the XMCD spectra were free from any experimental artifacts, the data were collected for both directions of the applied magnetic field, parallel and antiparallel to the x-ray beam. The degree of circular polarization of the monochromatic x-ray beam at the Ce $L$ edges was estimated to be $\sim 85\%$, whereas at the Mo $L_3$ and $L_2$ edges they were only $\sim 13\%$ and $\sim 5\%$, respectively. The x-ray absorption spectra for right and left circularly polarized x-ray beams, for both Ce and Mo, were then corrected individually for self-absorption effects, and the spectra at the $L_3$ edge were normalized to unity, whereas the spectra at the $L_2$ edge were normalized to one-half, respecting, therefore, the statistical ratio of 2/1. Finally, the XMCD spectra were corrected for the rate of circular polarization.

III. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structure of Mo$_4$Ce$_4$Al$_7$C$_3$—obtained from analysis of the single-crystal XRD results—was found to be triclinic (space group 2, $P\overline{1}$) with one formula unit per unit cell [Fig. 1(a)]. The nonequivalent atomic positions are distributed in special Wyckoff positions $2i$ (two Ce, two Mo, three Al, and one C atom), $1c$ (one C atom), and $1b$ (one Al atom). The final cell parameters resulting from the structural refinement are as follows: $a = 5.5517(5)\AA$, $b = 5.5797(5)\AA$, $c = 11.6848(10)\AA$, $\alpha = 81.157(4)^\circ$, $\beta = 85.827(4)^\circ$, and $\gamma = 60.250(4)^\circ$. The unit-cell volume is $310.51(5)\AA^3$. The whole structural parameters related to the triclinic phase are given in Table I. Details concerning the structural determination from the single-crystal XRD results are given in Appendix A.
TABLE I. Structural parameters obtained from structure refinement of Mo₄Ce₄Al₇C₃ single-crystal XRD results.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
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<tr>
<td>Chemical formula</td>
<td>Mo₄Ce₄Al₇C₃</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1169.13 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal size</td>
<td>0.029 × 0.174 × 0.333 mm</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>2 (P − 1)</td>
</tr>
<tr>
<td>Unit-cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 5.5517(5) Å</td>
<td>a = 81.157(4)°</td>
</tr>
<tr>
<td>b = 5.5797(5) Å</td>
<td>β = 85.827(4)°</td>
</tr>
<tr>
<td>c = 11.6848(10) Å</td>
<td>γ = 60.250(4)°</td>
</tr>
<tr>
<td>Volume</td>
<td>310.51(5) Å</td>
</tr>
<tr>
<td>Z</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>2i (0.670, 0.793, 0.087)</td>
</tr>
<tr>
<td>Ce</td>
<td>2i (0.339, 0.453, 0.145)</td>
</tr>
<tr>
<td>Al</td>
<td>2i (0.834, 0.898, 0.290)</td>
</tr>
<tr>
<td>C</td>
<td>2i (0.674, 0.155, 0.000)</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>6.252 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>18.691 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>509</td>
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</table>

Figure 2 shows STEM images of the Mo₄Ce₄Al₇C₃ along the [110] and [¯100] zone axes, along with SAED patterns, obtained from a single-crystal sample. In these micrographs, the Ce atoms appear brightest due to Z contrast; Mo and Al are less bright, and the lightest, C, is invisible. The crystal structure consists of a (Mo₂/₃Ce₁/₃)₂C layer and three Al-Ce layers. The (Mo₂/₃Ce₁/₃)₂C layer is basically the same as in the i-MAX phases, viz. the (Mo₂/₃Sc₁/₃)₂C layers in (Mo₂/₃Sc₁/₃)₂AlC [see Fig. 1(d)]. In other words, Mo₄Ce₄Al₇C₃ can be viewed as an i-MAX phase where the Al layers are replaced by a stack of (i) one Al layer with the same kagomé lattice as in an i-MAX phase [see Fig. 1(c)], (ii) one Ce-Al plane defined in Fig. 1(e), and (iii) a second kagomé-like Al plane simply shifted with respect to the first one. The shift of the latter is due to the introduction of the Ce-Al plane [see Fig. 1(b)] and results in the triclinic symmetry.

We also synthesized Mo₄Pr₄Al₇C₃ both as powder and single crystal, and found it to be triclinic, with the same structure as Mo₄Ce₄Al₇C₃. Figure 3 shows STEM images of Mo₄Pr₄Al₇C₃ along the [110] and [¯100] zone axes, with corresponding schematics, obtained from a powder sample.

In the powder samples of both RE phases, we also identified an orthorhombic polymorph (space group 20, Cc221) with two formula units per unit cell, see Fig. 4 and Table II, showing results for Mo₄Ce₄Al₇C₃. The differences between the two structures are in the A-layer stacking sequence along the c axis. Interestingly, the single crystals only crystallized in the triclinic structure. In contrast, the powder samples often exhibited stacking faults and locally alternating orthorhombic and triclinic sequences. XRD on the powder sample of Mo₄Ce₄Al₇C₃ is shown in Fig. 5(a). Apart from the two polymorphs found by STEM analysis, a (Mo₂/₃C₁/₃)₂AlC i-MAX and Mo₂C are also present. Quantification of phase content was not performed because the sample’s quality was not high. Instead, a simulated pattern based on the identified space groups is included, for comparison. XRD on a powder sample of Mo₄Pr₄Al₇C₃ together with the simulated pattern are correspondingly shown in Fig. 5(b). Here the impurity phases are (Mo₂/₃Pr₁/₃)₂AlC i-MAX and Mo₂C.

B. Vibrational properties

According to the Mo₄Ce₄Al₇C₃ crystal structure, the 18 atoms in the primitive cell give rise to 3 acoustic modes and 51 optical modes at the Γ point of the Brillouin zone. The
optical-phonon modes can be classified with the following irreducible representation:

\[ \Gamma_{\text{optical}} = 24A_g(\text{Raman}) + 27A_u(\text{IR}). \]

In Fig. 6(a) and Table III, the experimental Raman spectrum of Mo4Ce4Al7C3 is compared to the Raman-active vibrational modes predicted from the \textit{ab initio} calculations, allowing for both a determination of the corresponding atomic structures and accurate identification of 24 Raman modes. In addition to the 24 expected lines, see Table III, four extra lines were observed in the spectra at 117, 140, and 147 cm\(^{-1}\), with the last one, at 255 cm\(^{-1}\), overlapping more or less with the line at 257 cm\(^{-1}\). These additional lines suggest the existence of local structural disorder.

Based on our visualization of the vibrational modes, see Fig. 6(b), we conclude that (i) the low-frequency modes (<220 cm\(^{-1}\)) correspond to Ce and Mo vibrations, (ii) the Al vibrations are located in the midfrequency range (>220 cm\(^{-1}\)), and (iii) the high-frequency modes (>500 cm\(^{-1}\)) mainly involve the C and Mo atoms. This is congruent with the inverse proportionality between the vibrational frequency and the atomic mass, reported previously for other MAX phases [22].

C. Magnetization measurements

The temperature dependence of the magnetization (M) below 20 K, under a field of 1000 Oe applied parallel to the \( c \) axis, shows a steep increase at 10.5 K (inflection point) followed by a gradual saturation into a plateau down to 2 K (Fig. 7). Similar behavior is observed when \( H \) is perpendicular to \( c \), though with a signal that is more than ten times smaller (circles in Fig. 7). Below 7 K, a small hysteresis is observed.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Mo4Ce4Al7C3</th>
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<tbody>
<tr>
<td>Formula weight</td>
<td>1169.13 g/mol</td>
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<tr>
<td>Temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>20 (C222)</td>
</tr>
<tr>
<td>Unit-cell dimensions</td>
<td>( a = 9.7138 ) Å ( \alpha = 90^\circ )</td>
</tr>
<tr>
<td></td>
<td>( b = 5.5700 ) Å ( \beta = 90^\circ )</td>
</tr>
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<td></td>
<td>( c = 22.9623 ) Å ( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
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<tr>
<td>Al</td>
<td>8( c ) (0.8304 0.3307 0.6474)</td>
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<td>8( c ) (0.0860 0.0771 0.6468)</td>
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<tr>
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<td>8( c ) (0.5835 0.0846 0.6466)</td>
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<td>4( b ) (0.0000 0.6713 0.2500)</td>
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<td>4( a ) (0.6657 0.0000 0.0000)</td>
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<td>4( a ) (0.3390 0.0000 0.0000)</td>
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<td>Ce</td>
<td>8( c ) (0.8314 0.1718 0.2697)</td>
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<td>8( c ) (0.8341 0.1595 0.4261)</td>
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<tr>
<td>Mo</td>
<td>8( c ) (0.1718 0.1729 0.4561)</td>
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<td></td>
<td>8( c ) (0.4947 0.1709 0.4534)</td>
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</table>
FIG. 5. XRD on powder samples of (a) Mo₄Ce₄Al₇C₃ and (b) Mo₄Pr₄Al₇C₃, with respective simulated XRD patterns from the schematic cells shown in Figs. 2 and 3. Markers below the Exp. XRD indicate the peak position of Mo₄RE₄Al₇C₃, i-MAX, and Mo₂C.

between the FC and ZFC measurements. These observations are characteristic of a ferromagnetic (FM) phase transition at $T_C = 10.5$ K. More evidence for FM behavior is given by the M versus H curves shown in Figs. 8(a) and 8(b), which were obtained with H perpendicular and parallel, respectively, to the $c$ axis. The curves reveal a large anisotropy. When H is perpendicular to $c$, a large hysteresis is observed with coercivity $H_c = 0.23$ T. When H is parallel to $c$, a large magnetization with small hysteresis is observed, with $H_c = 0.03$ T. These results confirm that the easy magnetization axis is along the $c$ axis. The origin of the anisotropy is not clear at this stage.

In the paramagnetic state, above 20 K, the inverse susceptibility ($\chi$) deduced from the Arrott plot is presented in Fig. 9 (the larger uncertainty at higher temperatures reflects the weak M signal obtained in the small single-crystal sample used). In agreement with the Curie-Weiss law, $1/\chi$ varies linearly as $1/\chi = (T - \theta_p)/C_{th}$, where $\theta_p$ is the paramagnetic Curie temperature and $C_{th}$ is the theoretical Curie constant. Interestingly, the slope is inconsistent with the Curie constant for Ce$^{3+}$ ions (blue line, Fig. 9). At 2.18(8)$\mu_B$, the effective moment of the Ce$^{3+}$ ions—deduced from a linear fit of the dashed line in Fig. 9—is lower than the saturation moment expected from isolated Ce$^{3+}$ ions in the $4f^1$ configuration, viz. 2.54$\mu_B$. The dashed line shown in Fig. 9 that assumes a magnetic moment of 80 $\pm$ 3% is clearly a much better fit to the results. We thus conclude that only $\approx 80 \pm 3 \%$ of the Ce ions are in a +3 valence state. This conclusion is consistent with the results obtained by XANES discussed in the next section.

It should be noted that the presence of two Ce sites, with quite different coordination, could result in Ce sites with a +3 valence and Ce sites with a mixed valence +$(4 - \delta)$, in line with observations made for other compounds; see, e.g., [23]. Assuming a valence of +3 for one site, and using our magnetization data, one would expect a mixed valence of +3.28 for the other site. This value is comparable to the value of +3.36 obtained for 50% of the Ce sites—with longer bond lengths—in CeRuSn [23]. To appreciate the plausibility
TABLE III. Experimentally observed ($\omega_{\text{expt}}$) and calculated ($\omega_{\text{calc}}$) Raman modes in Mo$_4$Ce$_4$Al$_7$C$_3$. Asterisks denote additional lines.

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<th>$\omega_{\text{expt}}$ (cm$^{-1}$)</th>
<th>$\omega_{\text{calc}}$ (cm$^{-1}$)</th>
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<tr>
<td>355</td>
<td>350.9</td>
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<tr>
<td>503</td>
<td>512.9</td>
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<tr>
<td>558</td>
<td>554.1</td>
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<tr>
<td>630</td>
<td>617.9</td>
</tr>
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</table>

of this interpretation, the coordination of the Ce1 and Ce2 ions is illustrated in Figs. 10(a) and 10(b), respectively. Empirically, the bond strength between two atoms is inversely proportional to the distance between them. Therefore, we evaluate the interatomic (ionic) distance between the two Ce sites and their nearest atom neighbors. We define the empirical bond strength ratio as the interatomic distance divided by the sum of the covalent radii of Ce and the bonding atoms. In Fig. 10(c) we show the Ce1 sites and the bonding atoms with an empirical bond strength ratio smaller than 1.11. As can be seen, the Ce1 sites are closely bonded to Mo and C, and to a smaller extent to Ce2 ions. The same procedure is applied to the Ce2 atoms, as shown in Fig. 10(d). It appears that the Ce2 atoms are only strongly bonded to Ce1.

It is thus reasonable to conclude that the Ce1 ions are more strongly bonded to Mo and C. In the MAX phases, it is well established that the $d$ orbitals of the M atoms dominate at the Fermi level, see, e.g., Ref. [24], where the orbital nature of the Fermi level electrons is not only predicted, but also determined from angle-resolved photoemission spectroscopy (ARPES) measurements. We thus expect a stronger hybridization of the Ce1 atoms with the itinerant Mo atoms’ $d$ states, compared with Ce2. Such a mechanism is known to induce mixed valences in a number of compounds [25]. In our case, we have no definitive clue for assigning the mixed valence
FIG. 9. Inverse magnetic susceptibility (deduced from the Arrott’s plots) with H//c. The blue line represents the Curie-Weiss law curve obtained assuming 100% Ce$^{3+}$ ions, and the black dashed line assumes 80% Ce$^{3+}$ ions.

state to either of the two different sites. But, as discussed below, assuming that only one of the sites exhibits a mixed valence permits us to elaborate a consistent interpretation of the combined magnetization, XANES, and XMCD data.

The spontaneous M value deduced from Arrott’s plot at 4 K (H//c, graph not shown) gives 0.67μB per Ce ion. In this case, the spontaneous magnetic moment should reach 0.77μB per Ce atom at 0 K. This value is appreciably lower than the maximum value of 2.14μB expected at 0 K for the Ce$^{3+}$ ion. Part of this reduction could be ascribed to the crystalline electric field that partly lifts the degeneracy of the fundamental multiplet. However, and as reinforced by our interpretation of the XANES and XMCD data expounded in the next section, we suspect that only the Ce sites corresponding to a pure valence of +3 and 4$f^1$ configuration are ferromagnetic, whereas the Ce atoms with a mixed valence of the second site and 4$f^1$ configuration are paramagnetic. In this scheme, only half of the Ce atoms (those of the site with a pure 4$f^1$ configuration) would contribute to the spontaneous moment, giving 1.54μB, a more reasonable value, for Ce$^{3+}$ ions.

D. XANES and XMCD

In the ground state of mixed valence Ce compounds, the energies of the Ce 4$f^0$ (tetravalent Ce$^{4+}$) and 4$f^1$ (trivalent Ce$^{3+}$) configurations are close to each other and mixed by the hybridization between the 4$f$ electrons and the 5$d$ conduction-band states. In the final state of the Ce L$_3$ XANES, however, the energies of the two configurations are separated by a strong core-hole potential (of the order of 10 eV) acting on the 4$f$ state, so that the XANES spectrum exhibits two peaks. This is usually taken as evidence of the mixed valence state [26–29]. Analyzing the intensity ratios of the two peaks, we were able to estimate the average valence state of the Ce ions and the average Ce 4$f$ magnetic moment was quantitatively determined from the XMCD results (see below).

The XANES spectra recorded at the Ce L$_{3,2}$ edges of Mo$_2$Ce$_4$Al$_7$C$_3$ are shown in Fig. 11 (left axis). The spectra are dominated by the electric dipolar transitions (2$p$ → 5$d$). The main resonances (“white lines”) at the L$_3$ and L$_2$ absorption edges show a clear double peak structure, which as just noted is commonly identified as the signature of a mixed valence ground state [26–29]. The low-energy peak at ~5726 eV is related to the 4$f^1$ configuration, whereas the high-energy...
peak is assigned to transitions within the $4f^0$ configuration in the ground state of the Ce ions. A quantification of the electronic states can be obtained by estimating the relative spectral weights of the $4f^1$ and $4f^0$ features. A fitting procedure [30]—using a sum of two Lorentzians and two arctangent curves to decompose the Ce $L_3$-edge XANES—generally applied for such data analysis [31] was used here for this purpose. Following this procedure (see Appendix B), we estimate that the relative weight of the $4f^0$ configuration [defined as the ratio $4f^0/(4f^0 + 4f^1)$] is $\sim 25 \pm 5\%$, which corresponds to an average Ce $4f$ electron count of $0.75 \pm 0.05$.

Figure 12 (left axis) shows the XANES recorded at the Mo $L_{3,2}$ edges. At first glance, the spectral shape of the white line at the Mo $L_2$ edge is mostly composed of a single, broad peak located at 2522 eV. However, one can notice a weak shoulder located at higher energy ($\sim 2526$ eV), reflecting crystal-field splitting [32]. The overall white lines at the Mo $L_{3,2}$ edges are rather broad and point out the delocalized character of the Mo $4d$ electrons. This agrees with the predictions and experimental verifications made for previously studied MAX phases; see, e.g., Ref. [24].

Figure 11 (right axis) shows the XMCD spectra recorded at the Ce $L_{3,2}$ edges at 2.1 K under a 1 T magnetic field. The existence of a finite XMCD signal at both $L_3$ and $L_2$ edges confirms that the Ce ions are carrying a magnetic moment. The spectral shape of the XMCD signals is characteristic of a $4f^1$ system, as observed in CeRu$_2$Ge$_2$ [33] or CeH$_2$/Fe multilayers [34], and consequently demonstrates that the Ce atoms are the main source of magnetism in Mo$_4$Ce$_4$Al$_7$C$_3$. The magnetic field dependence of the maximum dichroic signal at the Ce $L_2$ edge (Fig. 13) confirms ferromagnetic ordering of the Ce $4f$ moments. It should be stressed that the observation of only one magnetic peak corresponding to the main $4f^1$ final state demonstrates that only this channel leads to ferromagnetism. In contrast, the Ce ions with a mixed valent state exhibit a double-peak XMCD spectrum as observed in highly hybridized Ce systems with $3d/4d$ ions, e.g., Ce(Pd$_{1-x}$Ni$_x$)$_3$ [35]. In our case, such a double-peak XMCD signal is not observed at the Ce $L_1$ edge, meaning that the Ce ions with a mixed valent state are not involved in the ferromagnetism.

The above interpretation is also supported by the observation of a rather strong XMCD signal at the electric quadrupolar transitions ($2p \rightarrow 4f$) located $\sim 7$ eV below the first XANES peak (Fig. 11). Even at the $L_2$ edge of Ce, those transitions are clearly observable as a shoulder in the XMCD signal. We can therefore propose a model in which two nonequivalent Ce sites are contributing differently to the magnetic properties. One site is occupied by Ce ions with localized $4f$ states featuring a $4f^1$ configuration and is responsible for ferromagnetism. Since Ce ions in CeAl$_2$ [36] and CeAl$_3$ are known to be $4f^1$, we tentatively suggest that it is the Ce atoms in Ce2 sites that are ferromagnetically coupled. The $4f$ states of the Ce1 site seem to be strongly delocalized and exhibit mixed valence behavior with Pauli-type paramagnetic response as observed in Ce(Pd$_{1-x}$Ni$_x$)$_3$ [35]. Our XMCD measurements were performed under a magnetic field of only

**FIG. 11.** Normalized XANES (left axis) and XMCD (right axis) spectra measured at the Ce $L_{3,2}$ edges on a Mo$_4$Ce$_4$Al$_7$C$_3$ crystal at $T = 2.1$ K and $H = 1$ T. The spectra have been corrected for self-absorption effects and circular polarization rates.

**FIG. 12.** Normalized XANES (left axis) and XMCD (right axis) spectra measured at the Mo $L_{3,2}$ edges in a Mo$_4$Ce$_4$Al$_7$C$_3$ crystal at $T = 2.1$ K and $H = 1$ T. Spectra have been corrected for self-absorption effects and circular polarization rates.

**FIG. 13.** Element-specific XMCD intensity vs $H$ measured at the Ce $L_2$ edge at $E = 6164.5$ eV at $T = 2.1$ K. A typical ferromagnetic behavior is observed, confirming the FM ordering of Ce $4f$ moments.
1 T, and this prevented us from observing double-peak XMCD from the latter site. Finally, we estimate the magnetic moment carried by Ce 4f electrons on a Ce2 site by comparing the experimental XMCD signals (see Fig. 11) with those recorded from the CeRu2Si2 ferromagnet carrying ∼1.5μB at magnetic saturation [37]. In the present case, the XMCD signal per Ce ion is about 2.6 times weaker, i.e., about 0.6μB, which is in good agreement with our macroscopic magnetization measurements. However, if we consider that only atoms on the Ce2 site carry a magnetic moment, it is approximately 1.2μB.

We also attempted to measure the magnetic properties of Mo atoms. Indeed, within the detection level of our measurements, no distinguishable XMCD signal was observed from Mo 4d electrons. Since the additional A layers substantially increase the interlayer spacing between the M layers, it would be interesting to verify if this enhances the quasi-2D character of these RE-based phases. In addition, the strongly correlated Ce 4f electrons and their probable hybridization with Mo 4d electrons may make the electronic structure intriguing [42,43]. ARPES measurements on Mo2Ce4Al7C3 single crystals are in progress.

IV. CONCLUSIONS

Herein we report on a family of layered RE compounds with a Mo2RE4Al7C3 chemistry, where RE = Ce and Pr. While powder samples of both phases crystallized in two polymorphs—triclinic (space group 2) and orthorhombic (space group 20)—the single-crystal samples crystallized solely in the triclinic structure. These 4473 phases are comprised of i-MAX blocks—viz. (Mo2/3)RE1(1/3)2C layers wherein the Mo and RE atoms are ordered—interleaved with three A layers comprised of Al and Ce atoms only.

The observed Raman modes of Mo2Ce4Al7C3 were in good agreement with DFT calculations. As for the MAX phases, the higher-energy modes are dominated by the C atoms occupying the octahedral sites between the Mo and Ce sites. Furthermore, below ∼10 K, the ground state is ferromagnetic. We also provide strong arguments based on x-ray spectroscopy that the two nonequivalent Ce sites exhibit different electronic and magnetic properties. The Ce2 site features localized 4f1 states with ferromagnetically ordered 4f moments of about 1.2μB, whereas the Ce1 site occupied by Ce ions with strongly delocalized 4f electrons are not involved in the ferromagnetism.

The discovery of any new layered magnetic material is noteworthy. However, since at this time there is no reason to believe that this family is restricted to Ce and Pr, and other RE elements—and quite possibly non-RE elements—this discovery is potentially quite important. The prospect of converting these 3D solids to their 2D analogs or MXenes is also quite exciting. We have recently shown that it is possible to etch both the Al and Sc atoms from the i-MAX phase (Mo2/3Sc1/3)2AlC. The fact that the A layers present between

<table>
<thead>
<tr>
<th>TABLE IV. Data collection and structure refinement for the Mo2Ce4Al7C3 single crystals.</th>
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<tr>
<td><strong>Theta range for data collection</strong></td>
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<td><strong>Index ranges</strong></td>
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<td><strong>Goodness-of-fit on $F^2$</strong></td>
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<td><strong>Final R indices</strong></td>
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<td><strong>Where</strong></td>
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<td><strong>Extinction coefficient</strong></td>
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<tr>
<td><strong>Largest diff. peak and hole</strong></td>
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<td><strong>rms deviation from mean</strong></td>
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the MX blocks are Al-rich bodes well for converting them to their 2D counterparts.

ACKNOWLEDGMENTS

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APPENDIX A: STRUCTURE DETERMINATION DETAILS

The integration of the data using a triclinic unit cell yielded a total of 57 227 reflections to a maximum redundancy 18.843, completeness 99.8%, $R_{int} = 3.42$%, $R_{wp} = 1.12$% and 3012 (99.18%) were greater than 2σ ($F^2$). Refinement leads to the final cell constants given in Table I. The ratio of minimum to maximum apparent transmission was 0.098. The calculated minimum and maximum transmission coefficients (based on crystal size) were 0.0620 and 0.6130. The structure was solved and refined with SHELXL, using the space group $P - 1$, with $Z = 1$ for the formula unit Mo$_2$Ce$_4$Al$_7$C$_3$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 80 variables converged at $R1 = 2.05$% for the observed data and $wR2 = 4.61$% for all data. The goodness-of-fit was 1.294. The largest peak in the final difference electron density synthesis was 3.331 e$^-$/Å$^3$ and the largest hole was $-2.336$ e$^-$/Å$^3$. On the basis of the final model, the calculated density was 6.252 g/cm$^3$ and $F(000), 509 e^-$. Details of the data collection and structure refinement are summarized in Table IV. Anisotropic atomic displacement parameters are summarized in Table V. Further information on crystal structure refinement is given in the cif files, which may be obtained from the Cambridge Crystallographic Data Centre, on quoting the depository numbers CCDC 1854775.

APPENDIX B: DECONVOLUTION OF THE XANES SPECTRA

For the determination of the valence state of the Ce atoms, we used a deconvolution technique proposed many years ago for intermetallic Ce compounds [30] (see Fig. 14). It assumes that the $L_3$ absorption spectrum of either a Ce$^{3+}$ or a Ce$^{4+}$ atom could be represented by a sum of an arc tangent function describing transitions from the 2$p$ core state into continuum and a Lorentzian function accounting for transitions into an unoccupied 5$d$ band of Ce. To fit the experimental spectrum, we used the same width of the Lorentzians and...
arctangent functions for both Ce valence states. The value of \( \approx 3.5 \) eV is determined by the core-hole lifetime [45]. The sum of the model spectra is normalized to unity. The energy positions of the Lorentzian maxima were chosen to coincide with the inflection points of the corresponding arctangent functions. The only two fitting parameters were the difference in energy between the two arctangent functions and the relative weight of the Ce atoms with the given valence state.