Synthesis and characterization of the new Ln$_2$FeMoO$_7$ (Ln = Y, Dy, Ho) compounds

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The new compounds Ln$_2$FeMoO$_7$ (Ln = Y, Dy, Ho) have been synthesized by solid-state reaction in evacuated silica tubes. The crystal structure of Dy$_2$FeMoO$_7$ and Ho$_2$FeMoO$_7$ was determined ab initio by simulated annealing in the R3 space group. Transmission electron microscopy study of Y$_2$FeMoO$_7$ revealed an unusual lamellar microstructure, composed of blocks with the structure of different zirconolite polymorphs. The dominant form corresponds to the zirconolite-2M type structure (space group C2/c) with a partially ordered array of Fe and Mo ions. X-Ray near edge spectroscopy data are consistent with formally Fe$^{3+}$ and Mo$^{5+}$ oxidation states for all compounds. Magnetic and transport measurements are reported.

Introduction

With the report of large negative magnetoresistance (MR) in the double perovskite Sr$_2$FeMoO$_6$, there has been a resurgence of interest in mixed B-site oxides, A$_2$B$_2$O$_6$O$_y$. The double perovskite Sr$_2$FeMoO$_6$, first reported in 1963 by Patterson et al., is a semimetal containing an ordered array of FeO$_6$ and MoO$_6$ octahedra and orders ferrimagnetically around 142 K.

In the present work, we attempted to modify the magnetic interactions between the Fe and Mo ions, from ferrimagnetic to ferromagnetic (FM), by changing the structural type from perovskite to pyrochlore. The pyrochlore structure, A$_2$B$_2$O$_6$O$_y$, contains a 3D network of corner-sharing BO$_6$ octahedra with a B–O–B bond angle ~135° interconnected with a network of A$_2$O$_y$ chains where the A cation is 8-coordinated (6-O and 2-O). For the double perovskite structure, the B–O–B bond angle is close to 180°. The change in structure from perovskite to pyrochlore can have a dramatic affect on the physical properties.

In example, for the perovskite CaMnO$_3$, the Mn$^{3+}$ ions order antiferromagnetically at ~125 K by Mn–O–Mn 180° (π-type) superexchange, whereas in the pyrochlore Ti$_2$Mn$_2$O$_7$, the Mn$^{3+}$ ions order ferromagnetically around 142 K, due to Mn–O–Mn π-type superexchange. Ti$_2$Mn$_2$O$_7$ has been reported to exhibit large MR effects around the FM ordering temperature. The discovery of large MR effects in this pyrochlore has led to the investigation of numerous pyrochlores with FM ordering. Examples of such compounds are the Mo$^{4+}$ pyrochlores, Ln$_2$Mo$_2$O$_7$ (Ln = Nd, Sm and Gd), which exhibit FM transitions below 100 K.7 Recently Taguchi et al. reported large negative magnetoresistance around 77 K in polycrystalline and single crystal Sm$_2$Mo$_2$O$_7$.8

In the present work we attempted to synthesize Ln$_2$FeMoO$_7$ pyrochlores with ordering of the Fe/Mo on the octahedral sites, with Ln = Y, Dy, Ho, and where the Fe–O–Mo bond angle would be sufficiently small, so that the superexchange interaction would be primarily of the π-type and lead to FM ordering. However, structural investigation revealed that these Ln$_2$FeMoO$_7$ compounds do not adopt the pyrochlore structure. In this paper we report the result of structural studies by combination of powder X-ray diffraction (XRD) and transmission electron microscopy. Magnetic susceptibility, resistivity and X-ray absorption near edge spectroscopy (XANES) data are also presented.

Experimental

Stoichiometric amounts of Mo powder (100 mesh, 99.95%, Alfa), MoO$_3$ (99.95%, Alfa), Fe$_2$O$_3$ (Fisher Certified) and the corresponding lanthanide oxide, Y$_2$O$_3$ (99.99%, Alfa), Ho$_2$O$_3$ (99.9%, Alfa) or Dy$_2$O$_3$ (99.9%, Alfa), were thoroughly ground and sealed in evacuated quartz tubes with a pressure of about 1 × 10$^{-5}$ Torr. The lanthanide oxides were heated at 1200 °C for 6 hours prior to use. The tubes were ramped up to 550 °C over a period of 2 hours, left isothermally for 12 hours, then heated slowly over a period of 8 hours to 1050 °C and held for 24 hours. Then the samples were quenched to room temperature, reground and sealed in a quartz tube at the same pressure as previously; the tubes were placed directly in a 1050 °C furnace for 24 hours to complete the reaction and quenched to room temperature. The resulting materials were black.

XRD data for Dy$_2$FeMoO$_7$ were collected with a Bruker D8 Advance Vario1 diffractometer (Bragg-Brentano geometry, CuK$_{\alpha 1}$ radiation, Ge(111) primary monochromator, position sensitive detector). Other XRD data were collected with a Bruker D9 Advance diffractometer (Bragg-Brentano geometry, CuK$_{\alpha 1}$ radiation, diffracted beam graphite monochromator, scintillation counter). All data were collected at 25 °C and are summarized in Table 1.

CCDC reference numbers 225101–225103.

See http://www.rsc.org/suppdata/jm/b3/b315028c/ for crystallographic data in CIF or other electronic format.

DC magnetic susceptibility measurements were made with a Quantum Design MPMS-XL SQUID magnetometer in different applied fields both in field cooled and zero-field cooled modes. Field-dependent magnetization measurements were performed with an applied field of −5 T < H < 5 T.

Temperature-dependent electrical resistivity measurements were carried out with a standard 4-point probe technique in a
Results and discussion

1. Crystal structure

1A. (Dy,Ho)2FeMoO7: X-ray diffraction. The X-ray diffraction patterns of all three compounds can be readily indexed in an R-centered hexagonal unit cell with lattice parameters of approximately \( \sqrt{2}a_t \) (~7.5 Å) and \( 2\sqrt{3}a_c \) (~17 Å), respectively, for a and c, where \( a_0 \) is the lattice parameter of the parent cubic fluoride cell. To our knowledge, there are no examples of compounds with this unit cell in the literature. A primitive hexagonal lattice (space group \( P\bar{3}m \)) with similar lattice parameters is found for the weberite structure (e.g., Na₂MnFeF₆). However, attempts at Rietveld refinement in the weberite model resulted in an overall poor fit to our observed data, with many significant violations of the R-lattice extensions; and the weberite model was rejected on these grounds.

A simulated annealing technique (Topas software) was applied for the Dy₂FeMoO₇ structure solution, and a stable refinement was achieved in the \( R\bar{3} \) space group (Fig. 1). The model was successfully applied to the Ho₂FeMoO₇ data as well. Lattice parameters and reliability factors are given in Table 1, refined atomic positions and isotropic atomic displacement parameters (ADPs) are summarized in Table 2, and selected interatomic distances are shown in Table 3. In all the refinements here and below, equal isotropic ADP values for all O atoms were assumed. The structure can be regarded as a distorted fluorite structure with the cations occupying “ideal fluorite” positions, and the distortion being associated with oxygen displacements and vacancy formation (in accordance with the O₂ stoichiometry). The Ln and Fe/Mo atoms form layers alternating along the c-direction. The lanthanide oxide layer is made up of ordered Ln(1) and Ln(2) ions which are coordinated to six (distorted octahedra) and eight (distorted cubes) oxygen atoms, respectively. In the Fe/Mo–oxide layer, the Fe/Mo(1) site is coordinated to six oxygen atoms forming distorted cubes and the Fe/Mo(2) sites form distorted octahedra, with two distant O atoms 2.50(6) Å (Ln = Dy) or 2.69(4) Å (Ln = Ho) away. These distorted octahedra share corners with each other, forming a network of three and six member rings along [001], similar to the sheets of octahedra.
parallel to the \{111\} layer in the pyrochlore structure, and typically referred to as hexagonal tungsten bronze (HTB) type slabs. There are two B-cation positions in the structure: 3a (000) and 9e (½00). The refinement of relative Fe/Mo occupancies is unstable, and in the final refinements equidistribution was assumed; which provides a good fit to the data with no anomalies in the ADP magnitudes.

Attempts to refine the structure of Y$_2$FeMoO$_7$ in the same $R\overline{3}$ model yielded anomalously high values of ADPs for all atoms (especially, B$_1$ $\sim$ 3.9(1) Å$^2$, B$_2$ $\sim$ 3.2(1) Å$^2$, B$_3$ $\sim$ 3.9(2) Å$^2$), indicative of the presence of static atomic displacements. On the other hand, a “pseudo-hexagonal” lattice is commonly encountered in monoclinic zirconolites. The diffraction patterns can be accordingly indexed in the $C2/c$ unit cell with the parameters

$$a_m \sim a \sqrt{6}, b_m \sim a \sqrt{2}, c_m \sim a \sqrt{11}/2$$

$\beta \sim 100^\circ$ (subscripts “c” and “m” indicate cubic fluorite subcell and monoclinic supercell, respectively), corresponding to the so-called zirconolite-2M structure. In this model, the “pseudo-hexagonal” description reveals the average substructure of the material. The monoclinic superstructure likely arises from the oxygen atom shifts and site vacancies (with respect to the MO$_2^-$ ideal fluorite stoichiometry), to which laboratory XRD is relatively insensitive; hence, no significant superlattice reflections were detected in the XRD pattern.

**1B. Y$_2$FeMoO$_7$: transmission electron microscopy study.** In order to remove the ambiguities of crystal symmetry of Y$_2$FeMoO$_7$, ED and HREM studies were undertaken. The ED patterns of the main zones are shown in Fig. 2, from left to right (100)$^*_H$, (100)$^*_H$ + (010)$^*_H$, (214)$^*_H$, and (001)$^*_H$, indexed using the hexagonal (H) unit cell derived from X-ray diffraction. The strongest reflections are those which correspond to this hexagonal unit cell. However, the weaker reflections cannot be indexed in this hexagonal cell, but can be indexed with the cell parameters $a \sim 12.8$ Å, $b \sim 7.4$ Å, $c \sim 11.5$ Å, $\beta \sim 100.7^\circ$ in space group $C2/c$ (see Table 1). The indexation in this unit cell is the one indicated on the ED patterns (Fig. 2). The relation between the hexagonal and monoclinic lattices is given by the transformation matrix

$$A_{H-M} = \begin{pmatrix} 2 & 1 & 0 \\ 0 & 1 & 0 \\ -1/3 & -1/6 & 2/3 \end{pmatrix}$$

which gives the following relations between the zone axis vectors: [110]$^*_H$, [100]$^*_H$, [010]$^*_H$, [001]$^*_H$, [214]$^*_H$, and [106]$^*_H$. The magnitude of monoclinic distortion of the pseudo-hexagonal lattice is extremely small (Table 1).

The second pattern consists of two overlapping ED patterns, one from the [010]$^*_H$ and one from [110]$^*_H$. This overlapping is clarified and confirmed by the Fourier transforms of different domains of the area selected for the pattern, which are shown as A and B in Fig. 5 (see later), and are the [010]$^*_H$ and [110]$^*_H$ zones, respectively. As can be seen from the HREM image in Fig. 3, domains of both orientations alternate over such short distances that the diffraction of a single domain cannot be isolated. Similarly, on the ED pattern denoted as [110]$^*_H$, which has minimum overlap from other zones among the patterns obtained, a faint presence of the [010]$^*_H$ zone can be observed.

The weaker reflections on the [106]$^*_H$ pattern are not superlattice reflections except those along [001]$^*_H$. These
weaker reflections do not belong to the zero order Laue zone, but are due to relrods of reflections from higher order Laue zones. The indices in parentheses (Fig. 4) indicate the corresponding reflection in the higher order Laue zone. For example the reflection at 1/6(661)* is due to the (110)* reflection. The reflections which are not shown on the scheme, but which do appear on the experimental pattern are due to twinning.

On the ED patterns streaking is present along the c*-direction. The origin of this streaking was unravelled with the aid of the HREM images (Fig. 3). In these images the presence of several different polytypes can be seen, especially when looking at the images at grazing angle. However, their presence was also established from the Fourier transforms of the selected regions, which are shown in Fig. 5. Each Fourier transform corresponds to an encircled area on the images (Fig. 3) which carries the same letter. The series of Fourier transforms show, from A to E (except A to B), an increase of the c cell parameter with steps of \( \sim 5.8 \text{ Å, i.e., A and B have } d_{001} = 11.3 \text{ Å, C has } d_{001} = 17.0 \text{ Å, D has } d_{001} = 22.6 \text{ Å and E has } d_{001} = 28.3 \text{ Å.} \)

The \( d_{001} = 17.0 \text{ Å parameter probably corresponds to a polymignte structure,}^{12} \text{ where } c \sim 17 \text{ Å is a parameter of a triple cell along the pseudohexagonal stacking axis. The } d_{001} = 22.6 \text{ Å parameter corresponds to zirconolite-4M polytype.}^{13} \text{ To our knowledge, no structural data for the } d_{001} = 28.3 \text{ Å polytype have been reported. The unit cell of the main phase (the one with } d_{001} = 11.3 \text{ Å) as seen along [010], is indicated in Fig. 3. The Fourier transform for C was taken from a different area of the same crystal, shown in the inset of Fig. 3. The positions of the reflections corresponding to the hexagonal sublattice remain the same for all polytypes. The simultaneous presence of the above polytypes with different c unit cell parameters is visible as streaking on the [010]* and [110]* diffraction patterns. The domains of the higher polytypes are too small to yield discernible SAED patterns. The inclusions of these higher polytypes in the main phase matrix can be only observed on the HREM images and their Fourier transforms.}

1C. \( \text{Y}_2\text{FeMoO}_7\): structure refinement and discussion. Based on the results of the ED and HREM study, refinement in the zirconolite-2M type model with the C2/cm space symmetry was undertaken for \( \text{Y}_2\text{FeMoO}_7\). The starting atomic positions were taken from ref. 14. Final Rietveld refinement was performed with Rietan 2000 software.\(^{15}\) Ionic scattering factors (i.e., Fe\(^{3+}\) and Mo\(^{5+}\), according to the XANES results, see below) were used, and the background was fitted by a 12-term Chebyshev polynomial. Anomalous broadening of the (004)\(_h\) = (006)\(_h\) reflection was observed, indicating a violation of ideal stacking
along (001)$_b$ on the micron scale, consistent with the HREM observations. This feature was introduced into the refinement through the partial profile relaxation.\textsuperscript{15} Preferred orientation with the March–Dollase vector $q = (001)^*$ was also introduced. Reasonable values of reliability factors were obtained (Table 1). However, the fit of some of the reflections, especially of (00l) type, is consistently poorer than the fit of the rest of the reflections. This likely reflects the presence of stacking faults as for the other zirconolite polytypes (see above). Refined lattice parameters and reliability factors are listed in Table 1, atomic positions and ADPs are summarized in Table 4, and selected interatomic distances are given in Table 5.

Bond Valence Sum (BVS) calculations was performed with the following parameters: for Fe$^{3+}$, $R_0 = 1.759$ Å and $B = 0.37$, for Mo$^{5+}$, $R_0 = 1.85$ Å and $B = 0.37$.\textsuperscript{17} In the present case BVS does not allow to identify the B-site distribution, because of close ionic radii of Fe$^{3+}$ ($CN = 6$, high spin) – 0.645 Å and Mo$^{5+}$ ($CN = 6$) – 0.61 Å.\textsuperscript{18} However, it can be used to test the overall correctness of the Rietveld refined model, as well as the valence assignment from XANES data. The values of 2.94 to 3.0 consistent with XANES data (see below). The values of 2.94 to 3.0 consistent with XANES data (see below).

Table 5 Selected bond distances (Å) for Y$_2$FeMoO$_7$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occupancy</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$\beta/\AA^2$</th>
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<tbody>
<tr>
<td>Y(1)</td>
<td>8(f)</td>
<td>1</td>
<td>0.3742(8)</td>
<td>0.1258(11)</td>
<td>0.4938(6)</td>
<td>0.61(1)</td>
</tr>
<tr>
<td>Y(2)</td>
<td>8(f)</td>
<td>1</td>
<td>0.1240(8)</td>
<td>0.1273(13)</td>
<td>0.4938(6)</td>
<td>0.61(1)</td>
</tr>
<tr>
<td>Fe/Mo(1)</td>
<td>8(f)</td>
<td>0.690/0.31(3)</td>
<td>0.251(12)</td>
<td>0.127(2)</td>
<td>0.7429(7)</td>
<td>1.84(4)</td>
</tr>
<tr>
<td>Fe/Mo(2)</td>
<td>8(f)</td>
<td>0.160/0.34(3)</td>
<td>0.503(3)</td>
<td>0.1152(5)</td>
<td>0.223(1)</td>
<td>1.04(5)</td>
</tr>
<tr>
<td>Fe/Mo(3)</td>
<td>8(e)</td>
<td>0.310/0.69(3)</td>
<td>0</td>
<td>0.138(2)</td>
<td>0.272(2)</td>
<td>2.7(5)</td>
</tr>
<tr>
<td>O(1)</td>
<td>8(f)</td>
<td>1</td>
<td>0.348(4)</td>
<td>0.153(6)</td>
<td>0.272(2)</td>
<td>1.9(2)</td>
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<td>O(2)</td>
<td>8(f)</td>
<td>1</td>
<td>0.473(5)</td>
<td>0.097(5)</td>
<td>0.057(3)</td>
<td>$\sim B$(O1)</td>
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<td>O(3)</td>
<td>8(f)</td>
<td>1</td>
<td>0.224(5)</td>
<td>0.134(5)</td>
<td>0.572(3)</td>
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<td>O(4)</td>
<td>8(f)</td>
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<td>0.123(6)</td>
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<td>0.079(5)</td>
<td>0.563(3)</td>
<td>$\sim B$(O1)</td>
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<tr>
<td>O(6)</td>
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<td>1</td>
<td>0.017(4)</td>
<td>0.143(6)</td>
<td>0.409(3)</td>
<td>$\sim B$(O1)</td>
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<tr>
<td>O(7)</td>
<td>8(f)</td>
<td>1</td>
<td>0.146(4)</td>
<td>0.010(6)</td>
<td>0.768(3)</td>
<td>$\sim B$(O1)</td>
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</table>

$^a$ Zirconolite-2M, C2/c model. ADPs for oxygen atoms were refined as common.
for Ti in the CaZrTi$_2$O$_7$ zirconolite$^{14}$ and higher than that found for Zn in Bi$_2$Zn$_{2/3}$Nb$_{4/3}$O$_7$.\textsuperscript{22}

It could be expected that similar structural distortions and corresponding specific microstructure might be also present in the other compounds studied here (Ln = Dy, Ho), and their apparent rhombohedral structures could be better described as a mixture of zirconolite polytypes on a local scale. However, an attempt at Rietveld refinement of their crystal structures with the same zirconolite-2M model as used for Y$_2$FeMoO$_7$ yielded unrealistic interatomic distances, including Fe/Mo1–O7 $\sim$ 1.47 and 1.62 Å for Ln = Dy and Ho, respectively.

### 2. Atomic oxidation states: XANES results

The oxidation states of the Fe and Mo ions for these samples were determined from the XANES data. Fig. 8 shows the Fe–K edges of the Ln$_2$FeMoO$_7$ samples along with a series of standard Fe–oxide spectra. The spectra of the Ln$_2$FeMoO$_7$ samples clearly lie between those of Fe$^{2+}$O and Sr$_3$Fe$_{4+y}$Co$_x$O$_7$. These results indicate that the Fe ions in the Ln$_2$FeMoO$_7$ samples are predominantly trivalent.

Fig. 9 shows the Mo–L$_3$ edges for Ln$_2$FeMoO$_7$, along with a series of standard compounds. The A and B features involve transitions into t$_{2g}$ and e$_g$ final states, respectively, and their relative intensities are indications of the hole count in these orbitals.\textsuperscript{23,24} Specifically, the intensity of the A feature increases relative to the B feature, as the Mo valence increases.

**Fig. 6** Polyhedral view of the zirconolite-2M (C$_2$/c) structure of Y$_2$FeMoO$_7$, with the Fe/Mo(1) octahedra shown in gray and Fe/Mo(3) octahedra in white. Y and Fe/Mo(2) atoms are represented as empty circles and black circles with white rims, respectively.

**Fig. 7** View of the (Fe/Mo)O$_6$ ab plane in the of the zirconolite-2M (C$_2$/c) structure of Y$_2$FeMoO$_7$, with Fe/Mo(1) octahedra shown in gray and Fe/Mo(3) octahedra in white. Y, Fe/Mo(2) and O(2) atoms are represented by the empty, black and gray circles, respectively.

**Fig. 8** Fe–K edge XAS spectroscopy of Ln$_2$FeMoO$_7$ (Ln = Y, Dy and Ho).

**Fig. 9** Mo–L$_3$ edge XAS spectroscopy of Ln$_2$FeMoO$_7$ (Ln = Y, Dy and Ho).
from 4+ to 6+. Moreover as the oxidation state of the Mo increases, the centrum of the combined A–B features exhibits a chemical shift to higher energy. The Ln$_2$FeMoO$_7$ Mo–L$_2$, spectra are intermediate between the Mo$^{5+}$ and Mo$^{6+}$ standards and very similar to the Mo$^{5+}$ double-perovskite Sr$_2$FeMoO$_6$ spectra. Thus, in Ln$_2$FeMoO$_7$ the Mo valence appears to be Mo$^{5+}$. The combined Fe and Mo XANES appear to support the assignment of Fe$^{3+}$/Mo$^{5+}$ as the “formal” oxidation states in these Ln$_2$FeMoO$_7$ compounds.

3. Magnetic and transport properties

Temperature dependence of the magnetic susceptibility for Dy$_2$FeMoO$_7$ and Ho$_2$FeMoO$_7$ closely follow a Curie–Weiss (CW) law with effective moments ($\mu_{\text{eff}}$) close to the theoretically calculated values in the entire temperature range. Small negative $\theta$ values obtained from the CW fits (Table 7) indicate that there are weak antiferromagnetic interactions present.

The magnetic susceptibility for Y$_2$FeMoO$_7$ shows appreciable difference between the zero-field-cooled and field-cooled data below $T_f$ ~ 20 K, Fig 10. The origin of this behavior is not clear yet; however, similar behavior has been observed before in other systems with mixed B-site cations, and traditionally attributed to a spin-glass-type transition resulting from frustrated magnetic interactions. The transition temperature decreases slightly with increasing applied field magnitude. Magnetization isotherms exhibit slight hysteresis below $T_f$ (Fig. 10, inset), however, the magnitude of the “hysteretic” component is very low.

Significant deviation from CW-type behavior was also observed for Y$_2$FeMoO$_7$ in the paramagnetic regime, and attempts of CW fits resulted in unrealistically low values of $\mu_{\text{eff}}$ and $\theta$. The $M(H)$ curves above $T_f$ are linear; and the Weiss constant estimate (see below) is close to zero; therefore the curvature of $\chi$ vs. $1/T$ plots can not be attributed to short-range correlation effects. A possible explanation for such behavior could be due to a ferromagnetic impurity (presumably, Fe metal) present in the sample in an amount below the detection level of X-ray diffraction. Measurements of the field dependence of magnetization showed characteristic linear $\chi$ vs. $1/H$ behavior in high (above saturation of Fe) fields, similar to that observed previously in Sr$_2$FeMoO$_6$. Since the magnetic susceptibility for Fe is expected to be weakly temperature dependent in the range of interest, $C$ and $\theta$ values have been obtained from $1/\chi = C/T$ vs. $T^2$ plots. The resulting curves are linear with good accuracy; however, the extracted value of $\mu_{\text{eff}}$ = 4.50 $\mu_B$ is still significantly lower than the theoretical one (6.16 $\mu_B$) for a Fe$^{3+}$ (d$^5$, high spin, $S = 5/2$) pair, and closer to the value (4.90 $\mu_B$) expected for a Fe$^{2+}$ (d$^6$, $S = 2$) pair. However, based on the combination of XANES and BVS results (see above) we conclude that the Fe ions are predominantly trivalent in the Ln$_2$FeMoO$_7$. There are several factors that could contribute to the observed discrepancy. First, our procedure of extracting the CW parameters could introduce systematic errors. Second, covalency effects, which are strong in oxide materials, mandate that transition metal ion states are superpositions of d-configurations, and it might manifest itself in a reduced value of the BVS for the Fe ion at the M2 site, see above. Consistent with this, there is a substantial controversy concerning the magnitude and even existence of ordered moment on Mo (and other 4d$^1$ and 5d$^1$ ions in ordered double perovskites from neutron diffraction studies (see refs. 19, 29 and references therein). No systematic variation of magnetic parameters as a function of magnetic field strength was observed.

Temperature dependence of resistivity for Ln$_2$FeMoO$_7$ is shown in Fig. 11. These materials are insulators down to ~150 K, and at lower T the magnitude of $\rho$ exceeds the limit of our device. The relatively large magnitude of resistivity ($\rho_{\text{RT}}$ ~ 20 0 cm) compared to the corresponding values in the double perovskites (e.g. in Sr$_2$FeMoO$_6$, $\rho_{\text{RT}}$ ~ 0.02 $\Omega$ cm), is attributed to the layered structure of this material favoring carrier localization, as well as significant disorder (with Fe/Mo mixing in the electronically active B-site). Consistent with the observed disorder, the data for Y$_2$FeMoO$_7$ and Ho$_2$FeMoO$_7$ can be adequately fit by a variable range hopping (VRH) model in the entire temperature range (200–350 K and 150–350 K, respectively), as shown in inset ‘A’ of Fig. 11. However,

![Fig. 10 Temperature dependence of the dc magnetic susceptibility for Y$_2$FeMoO$_7$ ($H = 1000$ Oe). Inset: magnetization isotherms for Y$_2$FeMoO$_7$ at $T = 5$ K and 50 K.](image)

![Fig. 11 Temperature dependence of the electrical resistivity for Y$_2$FeMoO$_7$ (●), Dy$_2$FeMoO$_7$ (●) and Ho$_2$FeMoO$_7$ (+). Insets A and B show $\rho$ vs. $1/T^2$ plots for Ho$_2$FeMoO$_7$ and Dy$_2$FeMoO$_7$, respectively. Positions of two weak anomalies are marked with arrows.](image)

### Table 7 Magnetic susceptibility and resistivity data for Ln$_2$FeMoO$_7$

<table>
<thead>
<tr>
<th></th>
<th>Y$_2$FeMoO$_7$</th>
<th>Dy$_2$FeMoO$_7$</th>
<th>Ho$_2$FeMoO$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{\text{exp}}$</td>
<td>4.50</td>
<td>17.6</td>
<td>16.3</td>
</tr>
<tr>
<td>$\chi_{\text{calc}}$</td>
<td>6.16</td>
<td>16.27</td>
<td>16.22</td>
</tr>
<tr>
<td>$\theta$ (K)</td>
<td>9</td>
<td>-36</td>
<td>-14</td>
</tr>
<tr>
<td>$\rho$ (Ω cm)</td>
<td>25</td>
<td>20</td>
<td>23</td>
</tr>
</tbody>
</table>

* Calculated effective moments are

$$\mu_{\text{eff}} = \sqrt[8]{2 \left( C (\text{Ln}^{3+}) \right) + C (\text{Fe}^{3+} (d^5)) + C (\text{Mo}^{5+} (d^1))}$$

with Curie constants $C_{\text{Y}} = 14.17$ and $C_{\text{Ho}} = 14.07$. For Y$_2$FeMoO$_7$, a modified Curie-Weiss fit is used to extract the magnetic parameters. Experimental $\mu_{\text{exp}}$ and $\theta$ for all compounds are averages of several measurements in different applied fields (no systematic field dependence of the observed parameters was detected).

because the range is quite limited, we were not able to reliably distinguish between various versions of Mott’s law with different exponents: $n = \frac{1}{4}$ (“conventional” 3D VRH), $n = \frac{1}{2}$ (2D VRH), and $n = \frac{1}{2}$ (Efros-Shklovskii modification with the Coulomb gap in the electronic density of states) yield nearly equally good fits, with a slight preference towards $n = \frac{1}{2}$. The temperature dependence of resistivity of Dy$_2$FeMoO$_7$ exhibits two weak anomalies (changes of slope in ln $\rho$–1/T^2 coordinates, as shown in inset “B” of Fig. 11) at $T \sim 190$ and 230 K, and the temperature dependence in the high-$T$ region is consistent with the VRH picture (with the same uncertainty concerning the choice of exponent). The origin of these anomalies is unclear thus far. There was no observed magnetic field dependence of the resistivity of any of the three studied compounds, consistent with the absence of magnetic order.

Conclusions

New compounds Ln$_2$FeMoO$_7$ (Ln = Y, Dy, Ho) were synthesized. The crystal structure of Dy$_2$FeMoO$_7$ and Ho$_2$FeMoO$_7$ was determined $ab initio$ by simulated annealing as a distorted fluorite-type structure with $R3$ symmetry. Transmission electron microscopy study of Y$_2$FeMoO$_7$ revealed an unusual lamellar microstructure, composed of blocks with the structure of different zirconolite polymorphs. The dominant form corresponds to the zirconolite-2M type structure (space group C2/c), and the structure was refined in this model from powder X-ray diffraction data. Rietveld analysis revealed the partial redistribution of B-cations over three non-equivalent sites, which was confirmed by Madelung sums calculations. XANES data are consistent with Fe$^{2+}$/Mo$^{5+}$ oxidation states. Y$_2$FeMoO$_7$ undergoes a spin-glass like transition around 20 K, while no magnetic transition was observed for Dy$_2$FeMoO$_7$ and Ho$_2$FeMoO$_7$. Resistivity measurement showed $\rho_{RT} \sim 20$ Ω cm and variable range hopping conduction.

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References

17. I. D. Brown, private communication.