Structure, phonons, and orbital degrees of freedom in Fe$_2$Mo$_3$O$_8$

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We report on the structural and spectroscopic characterization of the multiferroic Fe$_2$Mo$_3$O$_8$. Synchrotron x-ray and neutron diffraction, as well as thermal expansion measurements reveal a lattice anomaly at $T_N\approx60$ K but do not show any symmetry lowering in the magnetically ordered state. The lattice parameter $c$ exhibits a non-monotonic behavior with a pronounced minimum around 200 K, which is also reflected in an anomalous behavior of some of the observed infrared-active optical excitations and parallels the onset of short-range magnetic order, likely promoted by the quasi-2D nature of exchange interactions. The infrared reflectivity spectra measured between 5 and 300 K in the frequency range of $100-8000$ cm$^{-1}$ reveal most of the expected phonon modes in comparison with the eigenfrequencies obtained by density-functional calculations. The $A_1$ phonons show an overall hardening upon cooling, whereas a non-monotonic behavior is observed for some of the $E_1$ modes. These modes also show a strongly increased phonon lifetime below $T_N$, which we associate with quenching of orbital degrees of freedom on the tetrahedrally coordinated Fe$^{2+}$ site through constraining the orbital moment direction in the magnetically ordered state. A similar increase is observed in the lifetime of the higher-lying $d$-$d$ excitations of the tetrahedral Fe$^{2+}$ site, which become clearly visible below $T_N$ only.

I. INTRODUCTION

The transition-metal molybdenum oxides $A_2$Mo$_3$O$_8$ ($A$ = Mn, Fe, Co) exhibit a hexagonal structure in the polar space group $P6_3mc$ with the resulting polarization pointing along the $c$-axis [1–4]. The crystal structure of Fe$_2$Mo$_3$O$_8$ is illustrated in Fig. 1. The transition metal ions occupy two different sites with octahedral (Fe1) and tetrahedral (Fe2) coordinations, while the Mo$^{4+}$ ions are located at octahedrally coordinated sites. With the onset of antiferromagnetic ordering of the transition-metal ions, typically occurring between $T_N$ = 40−60 K [2], these compounds become multiferroics. In zero magnetic field, they realize either a collinear easy-axis antiferromagnetic or a ferrimagnetic state, as observed in Fe$_2$Mo$_3$O$_8$ [2, 5] and Mn$_2$Mo$_3$O$_8$ [5, 6], respectively.

The magnetic structure of Fe$_2$Mo$_3$O$_8$, with simultaneous antiferromagnetic ordering of the spins on the tetrahedrally and octahedrally coordinated sites, is displayed in Fig. 1. In the case of Mn$_2$Mo$_3$O$_8$, the ferrimagnetic order is realized by ferromagnetic ordering of the spins both at, respectively, tetrahedral and octahedral sites, with the two being antiparallel. These two states are in fact close in energy. In Fe$_2$Mo$_3$O$_8$, the ferrimagnetic spin arrangement can be induced by applying external magnetic field [7] or substituting Fe by non-magnetic Zn ions [4]. As a clear manifestation of the multiferroic character in the optical properties, magnetoelectric spin excitations were reported in Fe$_2$Mo$_3$O$_8$ [8] and in Zn-doped Fe$_2$Mo$_3$O$_8$, exhibiting an optical diode effect [9] and non-reciprocal gyrotropic birefringence [10], respectively.

Qualitatively, the multiferroic behavior of Fe$_2$Mo$_3$O$_8$ can be understood within the polar $P6_3mc$ symmetry of its room-temperature crystal structure without invoking symmetry lowering. However, a recent spectroscopic study pinpointed additional IR- and Raman-active, presumably phonon modes appearing below $T_N$, and interpreted them as a signature of symmetry lowering [11], although no direct measurement of the low-temperature crystal structure was attempted. Moreover, an ab initio study [12] failed to reproduce the antiferromagnetic order observed experimentally, thus raising the question whether the hexagonal room-temperature crystal structure is the right starting point for modeling the interesting physics of Fe$_2$Mo$_3$O$_8$, or effects like charge separation and Jahn-Teller distortions on Fe sites with tetra- and octahedral coordination should be taken into account.

In this study, we report on the crystal structure as well as electronic and vibrational IR-active excitations of Fe$_2$Mo$_3$O$_8$ as a function of temperature. Our structural data exclude a symmetry lowering with decreasing temperature, whereas subsequent band-structure calculations reveal orbital degrees of freedom that give rise to a sizable orbital moment on the tetrahedrally coordinated Fe site. These orbital degrees of freedom have unusual ramifications for the vibrational excitations, especially the $E_1$ phonon modes that show an unusual temperature dependence with a strongly increased lifetime in the magnetically ordered state. We thus establish orbital degrees of freedom of Fe$^{2+}$ as an important and previously overlooked ingredient of the Fe$_2$Mo$_3$O$_8$ physics.

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II. METHODS

Polycrystalline sample of Fe$_2$Mo$_3$O$_8$ was prepared by a repeated annealing of FeO (99.999 %) and MoO$_2$ (99 %) in evacuated quartz ampoules at 1000 °C. Fe$_2$Mo$_3$O$_8$ single crystals were grown by the chemical transport reaction method at temperatures between 950 and 900 °C with TeCl$_4$ as the transport agent. X-ray analysis of the crushed single crystals confirmed single phase of Fe$_2$Mo$_3$O$_8$.

X-ray and neutron diffraction experiments were performed on the polycrystalline sample. The neutron data were collected in the temperature range 1.7 – 275 K at the HRPT diffractometer of the Swiss Neutron Source (SINQ) at the Paul Scherrer Institute (Villigen, Switzerland) using neutrons with the 1.494 Å wavelength. The sample was placed inside a vanadium can and cooled down in the standard Orange cryostat. High-resolution synchrotron x-ray diffraction was performed at several temperatures between 25 K and 300 K at the MSPD beamline [13] of ALBA (Barcelona, Spain) using the wavelength of 0.3251 Å and the multi-analyzer detector. The powder sample was loaded into a spinning glass capillary and cooled down with the He-flow cryostat. The Jana2006 program [14] was used for the structure refinement.

Thermal expansion measurements were performed with the dilatometer described in Ref. 15 using a PPMS from Quantum Design. The length change along the $c$ direction of a hexagonal-shaped crystal was measured. The background contribution has been measured separately and subtracted from the raw data.

Reflectivity measurements were performed on an as-grown $ab$-plane single crystal and on an $ac$ cut mosaic sample composed of two single crystals. By using the Bruker Fourier-transform IR-spectrometers IFS 113v and IFS 66v/S equipped with He-flow cryostats, the frequency range from 100 to 8000 cm$^{-1}$ and the temperature range from 5 to 300 K could be covered. The temperature dependence of eigenfrequencies $\omega_0$ and dampings $\gamma$ of the phonon modes was analyzed by an oscillator model with the ReFFIT program developed by A. Kuzmenko [16, 17]. The optical conductivity was calculated from the reflectivity by Kramers-Kronig transformation with the $\omega^{-1}$ high-frequency extrapolation, followed by the $\omega^{-4}$ extrapolation for frequencies above 80000 cm$^{-1}$.

Band structures and orbital energies were obtained $ab$ initio from density-functional (DFT) calculations performed in the full-potential FPLO code [18]. Additionally, we employed VASP [19, 20] for calculating phonon frequencies using frozen displacements. The calculations were performed for the crystal structures refined at 1.7 K and 275 K. The Perdew-Burke-Ernzerhof exchange-correlation potential [21] was combined with the mean-field DFT+$U$ correction for correlation effects in the Fe 3$d$ shell. The on-site Coulomb repulsion $U_d = 5$ eV, Hund’s coupling $J_d = 1$ eV, and atomic-limit double-counting correction were applied following previous studies [22]. The calculated phonon frequencies are rather insensitive to the type of magnetic order, as well as to thermal expansion [23], but drastic changes in the phonon frequencies were observed when DFT was used instead of DFT+$U$, and a non-magnetic (spin-unpolarized) calculation was performed [23]. Such plain-DFT results reproduce the calculated phonon frequencies reported in Ref. 11, but show a quite poor agreement with the experiment [23].

III. RESULTS

A. Crystal structure

Both x-ray and neutron diffraction data are compatible with the hexagonal $P6_3mc$ symmetry at all temperatures down to 1.7 K. Neutron data showed increased intensities of several low-angle reflections, most notably 100, below $T_N$, whereas x-ray intensities remained unchanged (Fig. 2). This indicates that the onset of magnetic order in Fe$_2$Mo$_3$O$_8$ has only a weak influence on the crystal structure, and changes in the neutron data are mostly related to the magnetic scattering. Indeed, neutron diffraction data below $T_N$ were successfully refined using the same $P6_3mc$ model (Table I) along with the antiferromagnetic structure proposed in Ref. 2, where both Fe1 and Fe2 moments point along the six-fold axis (magnetic space group $P6'_3mc$). The in-plane components of the magnetic moments are zero within the sensitivity of our measurement and in agreement with the vanishing mag-
nnetic susceptibility measured in field applied along the c-axis [24].

The magnetic structure of Fe$_2$Mo$_3$Os entails the Fe1 and Fe2 moments as independent parameters. However, the refinement was not sensitive to their ratio, so we eventually constrained the two and arrived at 4.61(2) $\mu_B$ at 1.7 K in excellent agreement with the earlier work [2]. The ordered moment is somewhat higher than the spin-only value of 4 $\mu_B$ for high-spin Fe$^{2+}$, suggesting a sizable orbital contribution.

Neither atomic coordinates nor thermal displacement parameters showed any abrupt changes around $T_N$. The atomic coordinates are nearly constant within the temperature range of our study, whereas the displacement parameters systematically increase upon heating [23]. The in-plane lattice parameter $a$ also increases upon heating due to thermal expansion (Fig. 3a), but the out-of-plane lattice parameter $c$ reveals a rather unusual behavior with a minimum around 200 K and a kink at $T_N$ (Fig. 3b). This kink is even better visible in the linear thermal-expansion coefficient obtained from dilatometry (Fig. 3c).

A weak lattice anomaly at $T_N$ is not unexpected, but the minimum in the $c$ parameter at 200 K has no counterpart in thermodynamic or spectroscopic measurements reported so far. A closer inspection of the data suggested two further effects that appear below this temperature. First, reflection broadening becomes more anisotropic, as can be seen from the increase in the $S_{202}$ parameter (Fig. 3c) which accounts for the anisotropic contribution to the reflection width due to strain [25]. This parameter is non-zero even at room temperature but remains nearly temperature-independent down to 200 K, increases below this temperature, and saturates below $T_N$. The change in the peak width is hardly noticeable in the neutron data but can be recognized in the high-resolution synchrotron data that show slightly broader 4$\theta$ reflections below 200 K (Fig. 2d).

Second, neutron diffraction data collected right above $T_N$ show a broad diffuse feature around the position of the 100 reflection. This reflection then attains the largest magnetic contribution in the ordered state, so the broad feature represents magnetic diffuse scattering. It is gradually suppressed upon heating and fully disappears around 200 K, where the background of the neutron diffraction pattern develops a weak downward curvature typical of paramagnetic scattering (Fig. 3d).

These observations suggest that short-range magnetic order appears in Fe$_2$Mo$_3$Os below 200 K. Its formation may be linked to the minimum in the $c$ parameter, because the onset of spin-spin correlations will often facilitate lattice expansion if it leads to an increase in the exchange energy and stabilization of magnetic order [26]. The relation of the minimum in $c$ to the increase in the reflection broadening, $S_{202}$, is less obvious at this point, since anisotropic strain exists in the system even at room temperature. Such a broadening is usually caused by defects like antiphase boundaries or stacking faults, while its further increase below 200 K may be a mere consequence of the non-monotonic temperature evolution of the lattice parameter $c$ and does not indicate tendency toward symmetry lowering. Indeed, in systems with sym-

**TABLE I.** Structural parameters of Fe$_2$Mo$_3$Os at 1.7 K (upper rows) and 275 K (bottom rows), as determined from Rietveld refinements of the neutron diffraction data. The atomic displacement parameters $U_{iso}$ are given in 10$^{-2}$ Å$^2$. The lattice parameters are $a = 5.77499(2)$ Å, $c = 10.0636(1)$ Å at 1.7 K and $a = 5.78021(4)$ Å, $c = 10.0608(2)$ Å at 275 K, and the space group is $P6_3/mmc$. The refinement residuals $R_I/R_p$ are 0.009/0.034 at 1.7 K and 0.011/0.056 at 275 K, with the higher $R_p$ due to the lower statistics of the 275 K data.

| site | $x/a$ | $y/b$ | $z/c$ | $U_{iso}$ |
|------|-------|-------|-------|-----------|
| Fe1  | 2b    | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.95310(1) | 0.12(2) |
| Fe2  | 2b    | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.95315(1) | 0.12(2) |
| Mo   | 6c    | 0.146(1) | $-x$ | 0.25$^a$ | 0.25$^a$ |
| O1   | 2a    | 0      | 0     | 0.39048(1) | 0.29(4) |
| O2   | 2b    | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.14643(1) | 0.46(4) |
| O3   | 6c    | 0.4880(1) | $-x$ | 0.36299(2) | 0.29(2) |
| O4   | 6c    | 0.1665(1) | $-x$ | 0.63421(1) | 0.31(2) |

$^a$ Fixed to define unit cell origin

![FIG. 2. (a)–(d) Temperature evolution of the 100 (a,b) and 204 (c,d) reflections in the neutron (a,c) and synchrotron (b,d) data. Individual patterns are offset for clarity. (e) Rietveld refinement of the 1.7 K neutron data using the $P6_3/mmc$ symmetry of the crystal structure, with the tick marks showing peak positions and the line in the bottom showing the difference pattern. (f) Temperature evolution of the ordered magnetic moment ($\mu_{Fe1} = \mu_{Fe2}$) obtained from the neutron data.](image-url)
FIG. 3. (a)–(c) Temperature evolution of the lattice parameters (a,b) and strain parameter S_{202} (c) according to neutron diffraction data. (d) Temperature evolution of the magnetic diffuse scattering. (e) Linear thermal expansion coefficient \( \alpha = (1/L_0)(dL/dT) \) determined by dilatometry for \( \Delta L || c \).

Geometry lowering an anisotropic strain broadening will usually precede the symmetry-lowering phase transition and diverge upon approaching the transition from above [27]. This does not happen in Fe\(_2\)Mo\(_3\)O\(_8\), where the high-resolution synchrotron data collected both right above and well below \( T_N \) reveal only a weak broadening of the \( h0l \) reflections (Fig. 2d).

Regarding the transition at \( T_N \), it does not lead to any symmetry lowering either. Dilatometry reveals a weak thermal hysteresis around 60 K (Fig. 3e). On the other hand, the linear thermal expansion coefficient develops a \( \lambda \)-type anomaly typical of a second-order phase transition. Therefore, we interpret the transition at \( T_N \) as weakly first-order and exclude any significant structural changes upon the formation of the magnetically ordered state in Fe\(_2\)Mo\(_3\)O\(_8\).

B. Orbital degrees of freedom

We now use accurate crystallographic data to assess orbital degrees of freedom in Fe\(_2\)Mo\(_3\)O\(_8\) that features octahedrally and tetrahedrally coordinated Fe\(^{2+}\) with the \( d^6 \) electronic configuration. Both ions should be in a high-spin state according to the large magnetic moment they exhibit, and consequently possess orbital degrees of freedom when the octahedra and tetrahedra are not distorted. These orbital degrees of freedom may or may not be quenched in the real structure owing to weak distortions present therein.

Energies of the crystal-field levels in Fe\(_2\)Mo\(_3\)O\(_8\) are obtained from DFT by projecting the calculated band structure (FPLO) onto Wannier functions derived from Fe \( d \) states with suitable symmetries [28]. We find that the lower-lying triply-degenerate level of the octahedrally coordinated Fe\(^{2+}\) is split into the \( a_1 \) and \( e_1 \) manifolds, whereas the higher-lying doubly-degenerate level is not split [23]. Likewise, for the tetrahedrally coordinated Fe\(^{2+}\) the lower-lying doubly-degenerate level is not split, and the higher-lying triply-degenerate level undergoes the splitting (Fig. 4). The octahedral crystal-field splitting (\( \Delta_o \approx 0.68 \text{ eV} \)) is about twice larger than the tetrahedral crystal-field splitting (\( \Delta_t \approx 0.33 \text{ eV} \)), as expected from the atomic theory.

The quenching of orbital degrees of freedom hinges upon weak splittings of the triply-degenerate states. In the case of the octahedrally coordinated Fe\(^{2+}\), the \( a_1 \) level lies below the \( e_1 \) level and can be occupied by the minority-spin electron of Fe\(^{2+}\), so that orbital degrees of freedom are quenched. On the other hand, the minority-spin electron of the tetrahedrally coordinated Fe\(^{2+}\) remains on the doubly-degenerate \( e_1 \) level, with orbital degrees of freedom remaining unquenched. This qualitative analysis is corroborated by the full-relativistic DFT+U calculations that open a band gap of about 1.6 eV [23] and yield a large orbital moment of 0.5 \( \mu_B \) on the octahedrally coordinated Fe\(^{2+}\) and a negligibly small orbital moment of less than 0.01 \( \mu_B \) on the octahedrally coordinated Fe\(^{2+}\). The size of the orbital moment is comparable to the excess magnetic moment obtained by subtracting the spin-only moment of 4 \( \mu_B \) from the ordered moment of 4.61(2) \( \mu_B \) determined experimentally by neutron diffraction (Sec. III A), although in the latter case only the site-averaged magnetic moment is available.

C. Optical spectroscopy

Reflectivity spectra of Fe\(_2\)Mo\(_3\)O\(_8\) have been measured in the frequency range between 100 and 8000 cm\(^{-1}\) for two polarizations of the incoming light beam, \( E^\perp c \) and...
$E^\omega \parallel c$. Figure 5 shows the reflectivity for both polarizations at 5 and 100 K, i.e. for temperatures below and above the magnetic ordering temperature of $T_N = 60 \text{ K}$. At frequencies below 900 cm$^{-1}$, several excitation features including the phonon modes can be observed. Their temperature dependence will be analyzed in detail below. For frequencies around 3500 cm$^{-1}$ several excitations can be found that broaden considerably above $T_N$. These excitations can be ascribed to $d$-$d$ transitions of the tetrahedral Fe$^{2+}$ sites, which are commonly found in this frequency range [29–35], whereas the $d$-$d$ transitions of octahedral Fe$^{2+}$ are usually located at higher energies [36, 37].

**D. Far-infrared excitations and phonons**

The number and symmetry of the allowed zone-center IR active phonon modes for Fe$_2$Mo$_3$O$_8$ with space group $P6_3/mc$ [2] are given by the irreducible representations of the normal modes, of which the nine one-dimensional

$E^\omega \parallel c$. Figure 5 shows the reflectivity for both polarizations at 5 and 100 K, i.e. for temperatures below and above the magnetic ordering temperature of $T_N = 60 \text{ K}$. At frequencies below 900 cm$^{-1}$, several excitation features including the phonon modes can be observed. Their temperature dependence will be analyzed in detail below. For frequencies around 3500 cm$^{-1}$ several excitations can be found that broaden considerably above $T_N$. These excitations can be ascribed to $d$-$d$ transitions of the tetrahedral Fe$^{2+}$ sites, which are commonly found in this frequency range [29–35], whereas the $d$-$d$ transitions of octahedral Fe$^{2+}$ are usually located at higher energies [36, 37].

$A_1$-modes should be observable for $E^\omega \parallel c$ and the 12 doubly degenerate $E_1$-modes for $E^\omega \perp c$:

\[
\Gamma = 9A_1 + 12E_1 \quad \text{(Raman- and IR active)}
+ 13E_2 \quad \text{(Raman-active)}
+ A_1 + E_1 \quad \text{(acoustic)}
+ 3A_2 + 10B_1 + 3B_2 \quad \text{(silent)}.
\]

Figure 6 shows the FIR reflectivity spectra of Fe$_2$Mo$_3$O$_8$ for both $E^\omega \perp c$ and $E^\omega \parallel c$ at three selected temperatures. The optical conductivity calculated via Kramers-Kronig transformation from the 5 K reflectivity data is shown in Fig. 7. For $E^\omega \parallel c$, the reflectivity data above 150 cm$^{-1}$ has been used for the calculation.

In the following, we will distinguish three different types of excitation features in the FIR spectra, depending on the temperature range of their occurrence: (i) excitations visible already at room temperature, which are directly compared to IR active phonons of $A_1$ or $E_1$ symmetry, (ii) the spectral feature in the 600-
700 cm\(^{-1}\) range shown in detail in Fig. 6(c); this feature occurs below 200 K concomitantly with the minimum in the \(c\)-axis lattice parameter (see Fig. 3), and (iii) excitations observed only in the magnetically ordered state below \(T_N\) and indicated by the black arrows in Fig. 6.

All experimentally observed modes and the calculated phonon frequencies are summarized in Table II.

We start with the excitations of the first group and compare their frequencies with phonon eigenfrequencies obtained from DFT+\(U\) calculations. To this end, peaks in the experimental optical conductivity are used, as indicated in Fig. 7. Note that the features showing up at 215, 305, 335, and 520 cm\(^{-1}\) for \(E^\omega \parallel c\) (indicated by the green arrows in Fig. 7) stem from a slight polarization leakage of the \(E^\omega \perp c\) direction.

For \(E^\omega \perp c\) nine modes are observable below 800 cm\(^{-1}\) already at room temperature and can be compared to the twelve calculated eigenfrequencies of the expected \(E_1\) modes in the upper part of Table II. Similarly, for \(E^\omega \parallel c\) all observed eight modes present already at room temperature below 800 cm\(^{-1}\) are assigned to the expected \(A_1\) phonon modes. In the latter case, there is an excellent agreement between the experimental and calculated frequencies. Only for the lowest-lying \(A_1\)-mode, we cannot identify an experimental counterpart, because around 190 cm\(^{-1}\) there is an artefact resulting from our experimental setup. However, no mode was reported in this frequency range in Ref. [11].

For \(E^\omega \perp c\), the agreement for the \(E_1\) modes is still good but less favorable, and the counterparts of three modes could not be identified experimentally. The excitation features present around 850 cm\(^{-1}\) should not be considered as phonons, even if they are present already at room temperature for both polarizations and have been assigned to a one-dimensional representation \(A_1\) in Ref. [11]. First, these features develop a two-peak structure below 200 K (see Fig. 6(d)), where short-range magnetic order presumably sets in. Second, at the lowest temperatures the energy differences between the two modes (see Figs. 7(c) and (d) and Tab. II) are 13 cm\(^{-1}\) and 26 cm\(^{-1}\) for \(E^\omega \perp c\) and \(E^\omega \parallel c\), respectively. These splittings are of the same size as the ones observed for the electronic \(d\)-\(d\) excitations of the tetrahedral \(\text{Fe}^{2+}\) sites, which will be discussed below. This suggests that the excitations around 850 cm\(^{-1}\) are of electronic origin. Besides, no phonon eigenfrequencies were found in our calculations in this frequency range.

The temperature dependence of the modes below 800 cm\(^{-1}\) was obtained by fitting the reflectivity spectra with a sum of Lorentz and Fano oscillators for the complex dielectric constant,

\[
\epsilon = \epsilon_{\infty} + \sum_k \frac{\omega_{q,k}^2}{\omega_{q,k}^2 - \omega^2 - i\gamma_k \omega} \left(1 + i \frac{\omega_{q,k}}{\omega} \right)^2 + \left(\frac{\omega_{p,k} \omega_{q,k}}{\omega_{\text{pl},k} \omega} \right)^2
\]

Here \(\omega_{q}\) denotes eigenfrequency, \(\gamma\) the damping, and \(\omega_p\) the plasma frequency. \(\omega_{q}\) accounts for the asymmetry of the Fano oscillator, which was used to describe the asymmetric lineshapes of the four lowest-lying modes for \(E^\omega \perp c\) and for the 269 and 458 cm\(^{-1}\) modes for \(E^\omega \parallel c\). For \(\omega_{q} = 0\) the symmetric Lorentzian lineshape is recovered. The fano lineshape has been utilized to achieve a better fit for these six modes, but it is not clear at present, whether the asymmetry originates from the coupling to continuum background of other degrees of freedom or not. The values for the high-frequency dielectric constant \(\epsilon_{\infty}\) obtained at the lowest temperature are 7.6 for \(E^\omega \perp c\) and 5.8 for \(E^\omega \parallel c\).

For \(E^\omega \perp c\) at the highest temperatures the reflectivity was fitted with nine oscillators in agreement with the number of modes discernible at room temperature. Below 200 K, two additional oscillators were included to take into account the broad features in the region be-
TABLE II. Summary of experimental excitation frequencies (in cm\(^{-1}\)) measured at 70 K and 5 K. Upper part: Modes already visible at room temperature and corresponding values obtained from the DFT+U calculations (1.7 K crystal structure, antiferromagnetic order). Middle part: excitations concomitant with the onset of short-range magnetic order. Lower part: excitations concomitant with the onset of long-range magnetic order and appearing only below \(T_N\).

| \(E^\omega \perp c\) | \(E_1\) | \(E^\omega \parallel c\) | \(A_1\) |
|------------------|--------|------------------|--------|
| 70 K             | 5 K DFT+U | 70 K             | 5 K DFT+U |
| 135              | 129    | 162              | 201    |
| 218              | 214    | 223              | 371    |
| 290              | 292    | 312              | 458    |
| 333              | 335    | 351              | 558    |
| 454              | 452    | 455              | 643    |
| 473              | 471    | 481              | 782    |
| 510              | 514    | 522              | 782    |
| 561              | 559    | 577              | 782    |
| 751              | 754    | 750              |        |
| 836              | 837    | 831              | 830    |
| 850              | 850    | 857              | 856    |
| 613              | 596    |                  |        |
| 697              | 692    |                  |        |
| 270              |        | 230              |        |
| 426              |        |                  |        |
| 468              |        |                  |        |

tween 600 and 700 cm\(^{-1}\). To describe the modes emerging below \(T_N\), two additional modes were included. However, the mode at 468 cm\(^{-1}\) is too weak to be included in the fit (see Fig. 8). Similarly, for \(E^\omega \parallel c\) the modes listed in Table II were included in the fitting procedure, except for the ones at 230 and 447 cm\(^{-1}\), which have an extremely small spectral weight and are close to the experimental resolution limit. Finally, additional oscillators were included to account for the polarization leakage features.

Figure 8 shows representative fits of the experimental reflectivity data measured at 5 K for \(E^\omega \perp c\) and \(E^\omega \parallel c\) with the oscillator model described above. For both polarization directions the fit describes the experimental data quite well.

The temperature dependence of \(\omega_0\) and \(\gamma\) of the strongest phonon modes for \(E^\omega \perp c\) is shown in Figure 9. For all these modes clear anomalies of both \(\omega_0\) and \(\gamma\) can be found at \(T_N\). Above \(T_N\), the eigenfrequencies of some modes show a non-monotonic evolution in the temperature range between 150 and 200 K, correlating with the minimum observed in the \(c\)-axis lattice constant. The changes below \(T_N\) are even more pronounced. In particular, the damping \(\gamma\) of all these modes is abruptly reduced when entering the antiferromagnetically ordered phase. This overall decrease of \(\gamma\) at \(T_N\) is relatively strong, for the modes at the lowest frequencies the damping changes by one order of magnitude.

The temperature dependence of \(\omega_0\) and \(\gamma\) of the six strongest IR modes for polarization \(E^\omega \parallel c\) is shown in Fig. 10. In this polarization direction, the phonons are less affected by the magnetic ordering. Above \(T_N\), the eigenfrequencies of all modes monotonically increase with lowering the temperature, which is an expected behavior for anharmonic solids that stems from thermal expansion and phonon-phonon interactions [38–41]. Except the phonon mode located around 556 cm\(^{-1}\), the eigenfrequencies for \(E^\omega \parallel c\) experience either no or only slight changes at \(T_N\). The 556 cm\(^{-1}\) phonon reveals a drop in \(\omega_0\) below \(T_N\), however, in this case the nearly \(E^\omega \perp c\) active mode, which can be seen due to polarization leakage, hampers the fitting. In contrast to the \(E^\omega \perp c\) active modes, the damping \(\gamma\) shows an overall monotonically decreasing behavior with lowering temperature. Besides, \(\gamma\) is not significantly affected by the magnetic ordering and shows a smooth behavior upon crossing \(T_N\).

The hardening of the phonon modes upon cooling
FIG. 9. Temperature dependence of phonon eigenfrequency $\omega_0$ and damping $\gamma$ for $E^{\omega} \perp c$. The dashed vertical lines indicate the phase transition at $T_N = 60$ K.

is also in line with the DFT+$U$ results obtained for the 1.7 K and 275 K crystal structures. Most of the modes are expected to harden [23]. For example, the

frequencies of the $A_1$ modes should increase, on average, by 1 cm$^{-1}$, which is indeed observed experimentally (Fig. 10). A similar hardening trend is expected for the $E_1$ modes from the DFT+$U$ calculations, but most of them show a different behavior: some of them soften (135 and 290 cm$^{-1}$), some remain temperature-independent (218 and 510 cm$^{-1}$), or even behave non-monotonically (454 and 473 cm$^{-1}$) between 300 K and $T_N$. In fact, DFT+$U$ calculations for the antiferromagnetic spin configuration yield higher frequencies than in the ferromagnetic case [23]. Therefore, the onset of antiferromagnetic short-range order below 200 K should generally harden the $E_1$ modes, which is not the case for at least half of them. However, spin-phonon coupling [42] can lead to such effects already in the paramagnetic phase of exchange coupled systems, as reported, for example, for ferrimagnetic FeCr$_2$S$_4$ [43], or in frustrated spinel oxides [44].

FIG. 10. Temperature dependence of phonon eigenfrequency $\omega_0$ and damping $\gamma$ for $E^{\omega} \parallel c$. The dashed vertical lines indicate the phase transition at $T_N = 60$ K.
We now discuss additional modes appearing in the spectra below 200 K (group ii) and below $T_N$ (group iii). The broad feature appearing below 200 K and highlighted in Fig. 6(c) has been fitted with two Lorentzian oscillators. Fig. 11 shows the temperature dependence of their $\omega_0$, $\gamma$, and the total oscillator strength $\Delta \epsilon$. No phonons of suitable symmetry are expected in this frequency range, and the spectral feature is indeed much broader than the typical phonon resonance. Its overall intensity follows the increase in the $c$-lattice parameter (Fig. 3b) and becomes saturated below $T_N$, suggesting short-range magnetic order as the origin of this feature and magnetic degrees of freedom closely involved. The eigenfrequency (Fig. 11(a)) of the upper mode is nearly constant between 5 and 200 K within the experimental accuracy. For the lower-lying mode, $\omega_0$ exhibits a sudden drop when entering the antiferromagnetically ordered phase. The damping (Fig. 11(b)) of the lower mode is constant within the error bar. For the excitation with higher frequency, $\gamma$ increases with increasing temperature above $T_N$.

Finally, several additional modes are observed below $T_N$ only. Their frequencies are listed in the lower part of Table II. There are three additional modes for $E^\omega \perp c$ at 270, 426, and 468 cm$^{-1}$ and one additional mode at 230 cm$^{-1}$ for $E^\omega \parallel c$ (arrows in Fig. 6(a) and red dashed lines in Fig. 7). The eigenfrequencies and occurrence of these modes below $T_N$ are in agreement with the spectra reported in Ref. [11]. In comparison with the calculated eigenfrequencies of 286 cm$^{-1}$ and 475 cm$^{-1}$ without direct counterpart, the additional modes at 270 cm$^{-1}$ and 468 cm$^{-1}$ could correspond to two of the three missing $E_1$ modes of the hexagonal Fe$_2$Mo$_3$O$_8$ structure. However, the two other modes at 426 cm$^{-1}$ and 230 cm$^{-1}$ lie far away from any of the calculated frequencies without experimental counterpart. Since these modes appear at low temperatures only, it is tempting to assign them to a symmetry lowering below $T_N$ as suggested in [11], but our diffraction data exclude this scenario. A third possibility is that these additional excitations are of mixed nature, because excitations of electronic origin are also possible in Fe$_2$Mo$_3$O$_8$, as we discuss below.

**E. $d$-$d$ transitions in the mid-infrared**

We complete our spectroscopic characterization by analyzing MIR reflectivity spectra for $E^\omega \perp c$ and $E^\omega \parallel c$. The excitations observed between 3300 and 3700 cm$^{-1}$ (Fig. 12) can be ascribed to the $d$-$d$ transitions of the tetrahedral Fe$^{2+}$ ions [11], which are typically found in this frequency range [29–35]. The excitation energy yields $\Delta \epsilon \simeq 3500$ cm$^{-1}$ (0.43 eV), which is somewhat larger than found from DFT (0.33 eV), probably due to the correlation and multiplet effects neglected in the calculation.

For both polarization directions the $d$-$d$ transitions show up as sharp features in the reflectivity at low temperatures. With increasing temperature the $d$-$d$ transitions become gradually suppressed and considerably broadened when approaching $T_N$. Above $T_N$, the $d$-$d$ transitions remain visible as weak and broad features in the reflectivity spectra. Thus, the temperature dependence of the linewidth of the $d$-$d$ transitions strongly resembles that of the damping $\gamma$ for the phonon modes active for $E^\omega \parallel c$.

The $d$-$d$ transitions show a clear selection rule. For $E^\omega \perp c$ the spectrum is dominated by three excitations located at 3472, 3486 and 3498 cm$^{-1}$, while for $E^\omega \parallel c$ one excitation can be observed at 3447 cm$^{-1}$. The excitation energies have been determined from the maxima of the dielectric loss $\epsilon_2$, which is shown in Fig. 13 for $E^\omega \perp c$ (a) and $E^\omega \parallel c$ (b) for selected temperatures between 10 and 70 K.

The energies of the mid-infrared excitations observed in our spectra and in Ref. [11] are summarized in Table III. The most intense excitations observed in MIR are in agreement with the data reported in Ref. [11], but the additional sample-dependent broad excitation features in the reflectivity spectrum of Ref. [11] for $E^\omega \perp c$ around 3000 cm$^{-1}$ are absent in our spectra.

The presence of several $d$-$d$ transitions for $E^\omega \perp c$ stems from the fact that the energy levels shown in Fig. 4 are split by the spin-orbit coupling. The $\epsilon_1$ doublets produce five evenly spaced levels [45, 46] and generate multiple absorption lines that can be clearly resolved at temperatures below $T_N$. Three lines observed for $E^\omega \perp c$ are separated from each other by 13 cm$^{-1}$, while the line observed for $E^\omega \parallel c$ is separated from them by twice this value (26 cm$^{-1}$) as indicated in Fig. 13. In addition, the same energy separations have been observed in the FIR regime for the excitations in the range 830-860 cm$^{-1}$, generating an unusual set of electronic energy levels for the tetrahedral Fe sites. Note that an unusual level scheme had been addressed previously in connection with the interpretation of Mössbauer data [47].

These equidistant energy separations of 13 cm$^{-1}$ sug-
FIG. 12. MIR reflectivity spectra in the temperature range between 10 and 70 K for $E^\omega \perp c$ (a) and $E^\omega \parallel c$ (b) covering the frequency range of the $d$-$d$ transitions of tetrahedral Fe$^{2+}$.

FIG. 13. Dielectric loss $\epsilon_2$ for $E^\omega \perp c$ (a) and $E^\omega \parallel c$ (b) in the frequency range of the $d$-$d$ transitions of tetrahedral Fe$^{2+}$ for selected temperatures. Dashed lines indicate the energies of the $d$-$d$ excitations.

IV. DISCUSSION AND SUMMARY

Several scenarios have been proposed for Fe$_2$Mo$_3$O$_8$ in the recent literature. In Ref. 11, symmetry lowering was inferred from the additional, presumably phonon modes appearing at low temperatures, whereas the authors of Ref. 12 speculated on the possibility of an orbital ordering, which should also lead to a symmetry lowering. Alternatively, they put forward charge separation between the octahedral and tetrahedral sites as a microscopic mechanism that does not require symmetry lowering [12]. Our low-temperature structural data exclude all these possibilities. No signs of symmetry lowering have been observed down to 1.7 K. Moreover, the local environment of both Fe sites does not change with temperature and remains typical for Fe$^{2+}$. The absence of charge separation is confirmed by the bond-valence-sum (BVS) analysis of interatomic distances [49] that serves as a sensitive probe of Fe valence in mixed-valence oxides [50, 51]. Using experimental structural data at 1.7 K, we estimate BVS of 2.01 on the tetrahedrally coordinated site and 2.15 on the octahedrally coordinated site, which clearly

suggest that the fine structure of the levels originates from the lowest-lying electronic states split by spin-orbit coupling [45] as depicted in Fig. 4. In addition, a recent study of the low-energy excitation in Zn-doped Fe$_2$Mo$_3$O$_8$ revealed a vibronic excitation of the tetrahedral Fe$^{2+}$ ions with an onset at 12 cm$^{-1}$ [48], which strongly supports this assignment. From the spacing of $6\lambda^2/\Delta \nu = 13$ cm$^{-1}$ we estimate the spin-orbit coupling constant $\lambda \approx 87$ cm$^{-1}$, which is on par with other compounds containing Fe$^{2+}$ [34, 46].
rules out the Fe$^{3+}$–Fe$^{3+}$ scenario advocated by Ref. 12.

Our data also show that orbital degrees of freedom of the octahedrally coordinated Fe$^{2+}$ site are quenched by the trigonal distortion. This quenching does not occur for the tetrahedrally coordinated site, but in that case no Jahn-Teller distortion is expected either. Spin-orbit coupling lifts the degeneracy and creates a significant orbital moment that contributes to the ordered magnetic moment below $T_N$. With the experimental value of 4.61(2)$\mu_B$ at 1.7 K, the ordered moment clearly exceeds its spin-only value, thus confirming the formation of the orbital moment and, consequently, spin-orbit coupling as the primary mechanism lifting orbital degeneracy of the tetrahedrally coordinated Fe$^{2+}$ site in Fe$_2$Mo$_3$O$_8$.

Another, and perhaps less anticipated effect of the orbital degrees of freedom is the anomalous behavior of the $E_1$ phonon modes, including the non-monotonic temperature evolution of their frequencies and the abrupt increase in the phonon lifetime upon entering the magnetically ordered state. The fact that these features are only observed in the $E_1$ channel suggests their relation to the electronic levels of the $e_1$ symmetry, where orbital degeneracy occurs. Indeed, orbital fluctuations can occur through the fluctuating direction of the orbital moment. It should be parallel to the spin moment of Fe$^{2+}$, but otherwise is not constrained. In the absence of magnetic order, the orbital moment of Fe$^{2+}$ can point along $c$ or along $-c$, which are two different and distinguishable directions in the polar crystal structure of Fe$_2$Mo$_3$O$_8$. Internal fields that set in below $T_N$ fix the direction of the spin moment on a given Fe site and, therefore, quench orbital fluctuations. This quenching may affect the lifetime of the $E_1$ phonons.

Concerning the number of phonon modes, we identified eight out of the nine expected $A_1$-modes showing an excellent agreement with our DFT+$U$ calculation and nine out of twelve $E_1$ modes with a less satisfactory agreement. The additional weak modes in the range of 830-860 cm$^{-1}$ and the broad absorption feature at 600-700 cm$^{-1}$ undergo changes at around 200 K, indicating their relation to the minimum in the temperature dependence of the lattice parameter $c$ and the associated onset of short-range magnetic order. None of these modes can be interpreted as pure phonons. They probably have a combined vibrational and electronic origin.

The additional modes for $E^{\omega} \perp c$ and $E^{\omega} \parallel c$ observed below $T_N$ may not be pure phonons either, as magnetic degrees of freedom allow for combined phonon and magnon excitations. Moreover, it may be difficult to track experimentally, whether these modes are present in the magnetically ordered state only, or exist at all temperatures and simply become visible around $T_N$, because their lifetime increased, similar to the $E_1$ phonons (Fig. 9). In this case, a combination of electronic and phonon excitations becomes another plausible scenario. The splitting of the $e_1$ doublets (Fig. 4) creates low-energy excitations that are optically allowed [52] and couple to phonons, sometimes in a very intricate way [53]. An unambiguous assignment of these coupled modes appears to be difficult even for single Fe$^{2+}$ ions [53–55], let alone the concentrated Fe system of Fe$_2$Mo$_3$O$_8$ with additional magnetic degrees of freedom appearing below 200 K, where short-range magnetic order sets in. Our finding of similar energy separations of the $d$-$d$ excitations around 3500 cm$^{-1}$ and the excitations around 830-860 cm$^{-1}$ indicate an unusual electronic level scheme of the tetrahedral Fe$^{2+}$ sites, which might originate from vibronic couplings.

In summary, our crystallographic study of the Fe$_2$Mo$_3$O$_8$ multiferroic confirmed its robust hexagonal symmetry down to low temperatures. Orbital degrees of freedom are quenched on the octahedrally coordinated Fe$^{2+}$ site but remain active on the tetrahedrally coordinated site, where spin-orbit coupling generates a sizable orbital moment. The anomalous temperature dependence of the $E_1$ phonon modes with their largely increased lifetime in the magnetically ordered state also indicates the importance of orbital degrees of freedom, possibly via constraining the orbital moment direction in the antiferromagnetic state. The electronic excitations associated with the Fe$^{2+}$ ions on the tetrahedral sites suggest a splitting of the ground and first excited state by 13 cm$^{-1}$, in agreement with the direct observation of a low-energy mode, which was reported recently for Zn-doped Fe$_2$Mo$_3$O$_8$ and interpreted in terms of a vibronic excitation [48].

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### Supplemental Material

Structure, phonons, and orbital degrees of freedom in the Fe\textsubscript{2}Mo\textsubscript{3}O\textsubscript{8} multiferroic

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TABLE S1. Phonon frequencies calculated for crystal structures determined at different temperatures (1.7 K and 275 K) and for two different types of magnetic order, ferromagnetic and antiferromagnetic (experimental magnetic ground state). The nonmag stands for the uncorrelated non-magnetic calculation without the DFT+U correction.

|                | $T = 1.7$ K | $T = 1.7$ K | $T = 275$ K | $T = 1.7$ K | $T = 1.7$ K | $T = 275$ K |
|----------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                | nonmag     | FM          | AFM         | FM          | AFM         | FM          |
| $A_1$          | 724        | 792         | 787         | 789         | 784         | 789         |
|                | 694        | 733         | 734         | 730         | 730         | 730         |
|                | 547        | 653         | 651         | 653         | 651         | 653         |
|                | 461        | 568         | 558         | 565         | 563         | 563         |
|                | 423        | 456         | 454         | 455         | 452         | 452         |
|                | 387        | 453         | 444         | 453         | 447         | 447         |
|                | 275        | 363         | 365         | 363         | 365         | 363         |
|                | 236        | 267         | 262         | 267         | 264         | 264         |
|                | 154        | 207         | 201         | 207         | 203         | 203         |
| $A_2$          | 486        | 438         | 434         | 437         | 435         | 435         |
|                | 450        | 405         | 403         | 405         | 402         | 402         |
|                | 138        | 139         | 141         | 139         | 142         | 142         |
| $E_1$          | 691        | 744         | 750         | 742         | 745         | 745         |
|                | 558        | 570         | 577         | 567         | 570         | 570         |
|                | 522        | 520         | 522         | 518         | 520         | 520         |
|                | 490        | 482         | 481         | 482         | 480         | 480         |
|                | 449        | 471         | 473         | 467         | 467         | 467         |
|                | 437        | 450         | 455         | 450         | 448         | 448         |
|                | 307        | 347         | 351         | 346         | 351         | 351         |
|                | 295        | 318         | 312         | 319         | 313         | 313         |
|                | 221        | 273         | 286         | 274         | 282         | 282         |
|                | 195        | 219         | 223         | 218         | 222         | 222         |
|                | 163        | 186         | 191         | 187         | 189         | 189         |
|                | 146        | 157         | 162         | 157         | 159         | 159         |

$E_2$

|                | $T = 1.7$ K | $T = 1.7$ K | $T = 275$ K | $T = 1.7$ K | $T = 1.7$ K | $T = 275$ K |
|----------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                | nonmag     | FM          | AFM         | FM          | AFM         | FM          |
| $B_1$          | 739        | 824         | 815         | 821         | 812         | 821         |
|                | 707        | 739         | 738         | 736         | 734         | 736         |
|                | 540        | 650         | 647         | 648         | 648         | 648         |
|                | 483        | 594         | 586         | 593         | 591         | 593         |
|                | 427        | 491         | 481         | 492         | 483         | 492         |
|                | 377        | 450         | 449         | 448         | 446         | 448         |
|                | 290        | 356         | 363         | 355         | 362         | 355         |
|                | 212        | 251         | 253         | 251         | 253         | 251         |
|                | 167        | 212         | 208         | 213         | 212         | 213         |
| $B_2$          | 483        | 431         | 427         | 428         | 428         | 428         |
|                | 461        | 416         | 413         | 417         | 412         | 417         |
|                | 141        | 141         | 143         | 141         | 144         | 141         |

$E_2$
FIG. S1. Rietveld refinement of the synchrotron data collected at 25 K. Tick marks show reflection positions, and the line in the bottom is the difference pattern.

FIG. S2. Electronic density of states (DOS) for Fe$_2$Mo$_3$O$_8$: uncorrelated non-magnetic calculation (left) and a DFT+$U$+SO calculation with the ground-state antiferromagnetic spin configuration (right). The upper panels display total and atomic-resolved DOS. The middle and bottom panels display orbital-resolved DOS for Fe1 and Fe2, respectively, with only spin-minority channel shown in the DFT+$U$+SO case. Note that several bands in the vicinity of the Fermi level are of Mo 4$d$ origin and represent bonding and antibonding states of the Mo$_3$O$_{13}$ clusters.