Magnetic and vibronic THz excitations in multiferroic Fe$_{1.8}$Zn$_{0.2}$Mo$_3$O$_8$

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We report on optical excitations in the magnetically ordered phases of Fe$_{1.8}$Zn$_{0.2}$Mo$_3$O$_8$ in the frequency range from 10-110 cm$^{-1}$ (0.3-3.3THz). In the collinear easy-axis antiferromagnetic phase below $T_N = 50$ K eleven optically active modes have been observed in finite magnetic fields, assuming that the lowest-lying mode is doubly degenerate. The large number of modes reflects either a magnetic structure much more complex than in pure Fe$_2$Mo$_3$O$_8$ or that spin stretching modes become active in addition to the usual spin precessional modes. Their magnetic field dependence, for fields applied along the easy axis, reflects the irreversible magnetic-field driven phase transition from the antiferromagnetic ground state to a ferrimagnetic state, while the number of modes remains unchanged in the covered frequency region. We determined selection rules for some of the AFM modes by investigating all polarization configurations and identified magnetic- and electric-dipole active modes as well. In addition to these sharp resonances, a broad electric-dipole active excitation band occurs below $T_N$, which is not influenced by the external magnetic field. We assign this absorption band to a vibronic excitation related to the lowest-lying Fe$^{2+}$ electronic states in tetrahedral environment.

I. INTRODUCTION

The multiferroic compound Fe$_2$Mo$_3$O$_8$, which is known as the mineral kamikite$^4$, adopts a hexagonal unit cell with lattice constants $a = 5.777$ Å, $c = 10.057$ Å at room temperature as depicted in Fig. 1(a)$^2$. It belongs to the polar space group $P6_3mc$ with a polarization along the $c$ axis$^{3,5}$. The Fe$^{2+}$ ions occupy two different sites with tetrahedral (site $A$) and octahedral oxygen coordination (site $B$)$^5$. The two types of corner-sharing polyhedra form honeycomb-like layers in the $ab$-plane separated by breathing kagome layers of molybdenum octahedra as shown in Fig. 1(b). The Mo layers do not contribute to the magnetism due to spin-singlet formation of structural MoO$_3$ trimers$^6,7$. Fe$_2$Mo$_3$O$_8$ exhibits a collinear antiferromagnetic (AFM) order of the iron ions below the Nel temperature $T_N = 60$ K, which is accompanied by a strong increase of the polarization$^5$, giving rise to a type-I multiferroic state and strong magneto-optical effects$^8-10$. In addition, an applied magnetic field along the $c$ axis induces a ferrimagnetic (FiM) order$^2,4,6$. Recently, the possibility of additional orbital ordering on the Fe sites in both the AFM and the FiM state has been suggested by ab-initio calculations$^{11}$.

Isovalent substitution of Fe by nonmagnetic Zn in (Fe$_{1-y}$Zn$_y$)$_2$Mo$_3$O$_8$ has been reported to influence the magnetic phase diagram, leading to a stabilization of the ferrimagnetic phase with increasing Zn content$^{12,13}$. Previous studies revealed that the Zn$^{2+}$ ions predominantly occupy the tetrahedral sites for $y \leq 0.5$.$^6,14$

In this study we investigated the low-energy excitations in single crystals of Fe$_{1.8}$Zn$_{0.2}$Mo$_3$O$_8$ by THz spectroscopy. The temperature dependence of the magnetic susceptibility measured in 1 T shown in Fig. 2(a) exhibits a maximum at $T_N = 50$ K associated with the antiferromagnetic ordering.$^2,4,12$ The transition from the antiferromagnetic to the ferrimagnetic state for this Zn concentration can be realized in applied magnetic fields $H \parallel c$ of about 3-4 T (see Fig. 2(b)) at 13 K.

The magnetization measured at 13 K exhibits a two-step feature in the transition region characterized by the critical fields $H_{c1} = 3$ T and $H_{c2} = 3.8$ T as indicated in Fig. 2(b). This behaviour is in agreement with reported magnetization results for $y = 0.1$.$^{12}$ The zero-field cooled AFM state is driven irreversibly to a metastable FiM state by the magnetic field. Clearly, the width of the hystereses curves increases with decreasing temper-
measurements in the frequency range from 10-150 cm$^{-1}$ were performed by THz time-domain spectroscopy using a Toptica TeraFlash spectrometer and an Oxford Instruments Spectromag cryomagnet in external magnetic fields ranging from -7 T to 7 T in an ac-cut sample with a thickness of $d = 1.48$ mm and an ab-cut sample with $d = 0.6$ mm.

III. EXPERIMENTAL RESULTS

Temperature dependent polarized absorption spectra

The temperature dependence of the THz absorption spectra for the polarization configurations $E^\omega \parallel c$, (ab-cut sample) and the configurations $E^\omega \perp c$, $H^\omega \perp c$ and $E^\omega \parallel c$, $H^\omega \perp c$ (ac-cut sample) are shown in Fig. 3(a)-(c), respectively. Above $T_N$, there are no detectable excitations. The strong monotonous increase in absorption with increasing frequency for $E^\omega \perp c$ can be attributed to the low-energy tail of the lowest-lying infrared-active phonon of $E_1$ symmetry with an eigenfrequency of 130 cm$^{-1}$. The decreasing absorption of this contribution with decreasing temperature is in agreement with the strong narrowing of the IR-active phonon, when the system is cooled below $T_N$. Note that the lowest lying IR-active phonon for $E^\omega \parallel c$ is located at around 200 cm$^{-1}$ and, therefore, the frequency range where transmission can be detected is wider than for $E^\omega \perp c$ polarization. Upon cooling below $T_N$, several new modes emerge or become observable due to the reduced absorption of the IR-phonon contribution in the investigated frequency range. Since all of these modes seem to gain intensity and sharpen upon cooling we assign them to new excitations of the magnetically ordered state.

| mode | $\omega_0$ [cm$^{-1}$] | $E^\omega \perp c$ | $E^\omega \parallel c$ | $H^\omega \perp c$ | $H^\omega \parallel c$ | activity |
|------|----------------|-----------------|----------------|----------------|----------------|----------|
| $V_1$ | 23 | ✓ | ✓ | ✓ | E$^\omega \perp c$ | E$^\omega \parallel c$ |
| $EM_1$ | 44 | ✓ | ✓ | ✓ | E$^\omega \perp c$ | E$^\omega \parallel c$ |
| $M_1$ | 68 | ✓ | × | ✓ | H$^\omega \perp c$ | H$^\omega \parallel c$ |
| $M_2$ | 90 | ✓ | n.r. | ✓ | H$^\omega \perp c$ | H$^\omega \parallel c$ |
| $M_3$ | 96 | n.r. | n.r. | ✓ | ? | ? |
| $M_4$ | 114 | n.r. | n.r. | ✓ | ? | ? |
| $EM$ | 40 | ✓ | ✓ | ✓ | E$^\omega \perp c$ | E$^\omega \parallel c$ |
| $MM_1$ | 90 | ✓ | × | ✓ | H$^\omega \perp c$ | H$^\omega \parallel c$ |

TABLE I: Upper part: Selection rules for the excitations found in Fe$_{1.8}$Zn$_{0.2}$Mo$_3$O$_8$ for the different polarization configurations as shown in Fig. 3. The notation ✓ and × indicates the presence or absence of a mode. The cases when no observation was possible are denoted as n.r. (not resolved). Lower part: reported excitations in the AFM phase of pure Fe$_2$Mo$_3$O$_8$ at 4.5 K taken from Ref. 8.

Note that the high-frequency part of some spectra is
as well as in the ac-cuts. This is true for the (Fe_{1-\delta}Zn_{\delta})_2Mo_3O_8 series. For EM1 our data does not allow to exclude a difference in intensity for the two configurations, because the maximum of EM was not resolved. However, the eigenfrequency and the selection rule for EM1 are in agreement with a reported excitation called EM in pure Fe_2Mo_3O_8 (see Table I). In addition, EM1 was not observed for a Zn concentration of y = 0.125, where the AFM phase is completely suppressed and the ground state is ferrimagnetic.

In contrast to modes V_1 and EM1, the four additional modes, M_1-M_4, observed at higher frequencies can be excited for \( H^\omega \perp c \) and are thus considered to be magnetic dipole active. An additional electric-dipole activity is discarded for excitation M_1, because it does not appear for the configuration \( E^\omega \perp c, H^\omega \parallel c \). For modes M_2-M_4 our spectra for \( E^\omega \perp c, H^\omega \parallel c \) do not allow...
us to unambiguously exclude an electric-dipole activity, but we expect any such contribution to be weak. Note, that a magnetic-dipole active mode (named $MM_1$, see see Table I) with an eigenfrequency close to $M_2$ has been reported for $x = 0$ and $x = 0.125$, previously$^8$ and determined to be only magnetic-dipole active. Modes $M_1$, $M_3$, and $M_4$ have not been observed before, probably due to the low intensity of $M_1$ and the fact that the frequency range of $M_3$ and $M_4$ was not resolved in previous studies.

**Magnetic field dependent absorption spectra**

The magnetic field dependence of the absorption spectra for the three possible polarization configurations measured for $H \parallel c$ are shown in Fig. 4(a)-(c). Since the transition to the ferrimagnetic state occurs when the magnetic field is parallel to the c-axis, the $ab$-cut sample was measured in Faraday configuration ($H \parallel c$, $k \parallel c$) and the $ac$-cut in Voigt configuration ($H \parallel c$, $k \perp c$), where
$k$ is the wave vector of the incoming THz beam. Spectra measured with $H \perp c$ (not shown here) exhibited no field dependence of the absorption spectra.

The measurements were performed at 13 K, where the critical fields $H_{c1}$ and $H_{c2}$ of the magnetization steps and the saturation magnetization (see Fig. 2(b)) of the compound were accessible using our experimental setup. When increasing the magnetic field in the antiferromagnetic phase (blue spectra) we observe a linear splitting of the modes $M_1 - M_4$ as indicated by the black lines in Fig. 4(b) in Voigt configuration and for $M_1$ also in Faraday configuration (Fig. 4(c)). The corresponding effective $g$-factors for both branches are given in Fig. 4(e) and (f). The behaviour of $M_2$ in Faraday configuration is more complex, as a low-frequency satellite $M_5$ seems to emerge and soften with increasing field up to $H_{c2}$. For the electric-dipole active mode $EM_1$ no shift or splitting with increasing magnetic field could be resolved, but it loses intensity when approaching the transition region to the FIM state and it finally disappears for $H > H_{c2}$ (spectra for $H_{c1} < H < H_{c2}$ are shown in green, for $H > H_{c2}$ in red). This behaviour is in agreement with the corresponding $EM$-mode in pure Fe$_2$Mo$_3$O$_8$\cite{8}. Above $H_{c2}$ modes $M_1 - M_4$ also vanish, and new modes appear in the ferrimagnetic phase. We want to emphasize that the coexistence of modes of the AFM and FIM phases for $H_{c1} < H < H_{c2}$ indicates a two-phase regime in this field region. These new modes also show a field dependence and are labeled $F_1 - F_{11}$. A detailed comparison of the splitting of the antiferromagnetic modes at 2 T and the shape of the ferrimagnetic modes at 7 T is given in Fig. 5. Notably, the broad band $V_1$ does not exhibit any significant changes with increasing magnetic fields and does not seem to be influenced by the transition to the FIM state.

The resonance frequencies of the ferrimagnetic modes $F_1 - F_{11}$ either increase or decrease linearly with increasing magnetic fields as shown in Fig. 4. Additionally, we included the resonance frequencies of modes $F_1 - F_{11}$ measured upon lowering the magnetic field to zero (spectra not shown here) as open symbols in Fig. 4(d)-(f). The eigenfrequencies of $F_1$ and $F_2$ were found to cross each other below $H_{c1}$. The eigenfrequencies of $F_1 - F_{11}$ in the zero-field FIM state are given in Table II, together with the effective $g$-factors. In the lower part of Table II we list all reported modes of the FIM phase for (Fe$_{1-y}$Zn$_y$)$_2$Mo$_3$O$_8$ for a comparison. For $y = 0$ and $y = 0.125$ a magnetic-dipole active mode (called $\nu_2$ or $MM_2$) with a similar eigenfrequency as $F_1$ has been reported\cite{8}. For $y = 0.25$ and $y = 0.4$ this mode $\nu_3$ seems to have developed an additional electric-dipole activity\cite{9}. The additional modes $\nu_1$, $\nu_2$, and $\nu_3$ at lower frequencies cannot be directly related to the modes observed in our study, as we expect a continuous evolution of the modes with increasing Zn content and, therefore, consider the reported spectra for $y = 0$ and $y = 0.125$ as the most relevant.

IV. DISCUSSION

Modes $EM_1$ and $M_1 - M_5$ of the AFM phase

As already mentioned above, modes $EM_1$ and $M_2$ have been reported already for pure Fe$_2$Mo$_3$O$_8$ and interpreted as precessional modes of the collinear AFM structure, both being doubly degenerate modes\cite{8}. While the degeneracy of $M_2$ is clearly lifted in the external magnetic field with $g_{e,f} = 1.7$ for $H^\parallel c$, the double nature of $EM_1$ still remains to be confirmed in higher magnetic fields. The respective electric and magnetic dipole activity of the two modes was assigned to an inverse Dzyaloshinskii-Moriya mechanism and different single-ion anisotropies of tetrahedral and octahedral sites\cite{8}.

As our spectra reveal three additional magnetic modes $M_1, M_3, M_4$, we have to take into account that the disorder induced by substitution of iron by zinc may result in an increased number of nonequivalent tetrahedral Fe sites. In early Mubauer studies for various zinc dopings at least four different tetrahedral iron sites with different hyperfine fields could be distinguished\cite{10}. Given the absence of $M_1$ in the spectra of pure Fe$_2$Mo$_3$O$_8$ and the low intensity of the mode, we assume that this mode is due to the Zn induced disorder. As the spectral range reported for Fe$_2$Mo$_3$O$_8$ was limited to about 94 cm$^{-1}$, it is not clear, whether $M_3$ (at 96 cm$^{-1}$) and $M_4$ (at 114 cm$^{-1}$) are also disorder-induced modes or whether they are present in pure Fe$_2$Mo$_3$O$_8$, too. Preliminary THz measurements on pure Fe$_2$Mo$_3$O$_8$\cite{11}, however, indicate that $M_3$ is an intrinsic mode of Fe$_2$Mo$_3$O$_8$, while $M_3$ is not present in Fe$_2$Mo$_3$O$_8$ and results from Zn substitution. Under these assumptions, we conclude that at least the three modes $EM_1, M_2, M_4$ are to be regarded inherent to the magnetic structure of the pure compound and the two doubly degenerate mode $M_1, M_3$ may emerge due to the dilution of the magnetic iron sites by nonmagnetic zinc. Since mode $M_5$ shifts to lower eigenfrequencies with increasing magnetic field and disappears above $H_{c2}$, its behavior may be interpreted as a soft mode of the magnetic phase transition. However, its relation to $M_2$, from where it seems to originate, remains unresolved at present. Besides the influence of different Fe sites, the large number of magnetic modes may also be due to additional spin stretching modes\cite{20,21}.

Moreover, we want to mention that nonreciprocal directional dichroism could occur in the AFM phase, if the external magnetic field is applied perpendicular to the $c$-axis in Voigt configuration. A comparison of modes $M_1$ and $M_2$ measured in ±7 T did, however, not show any significant effects.

Modes of the ferrimagnetic phase

At present we identify eleven modes $F_1 - F_{11}$ in the spectra of the FiM phase for all measured polarization configuration above $H_{c2}$ (see Tab. II). In principle, this
TABLE II: Selection rules for the excitations $F_1 - F_{11}$ found for the different polarization configurations at 13 K as shown in Fig. 3. The eigenfrequencies $\omega_0$ correspond to the zero-field values in the FiM phase. The sign of the effective g-factor indicates the sign of the linear slope with increasing magnetic field. The notation $\checkmark$ and $\times$ indicates the presence or absence of a mode. The cases when no observation was possible are denoted as n.r. (not resolved). The lower part of the table lists reported modes of the FiM phase for different Zn concentrations taken from Refs. 8-10.

| mode                | $\omega_0$ ($H^\text{dc} = 0$ T) | g-factor | $ab$-cut | $ac$-cut | activity |
|---------------------|----------------------------------|----------|----------|----------|----------|
|                     | $[\text{cm}^{-1}]$               |          | $E_\omega, H_\perp \perp c$ | $E_\omega \perp c, H_\parallel \parallel c$ | $E_\omega \perp c, H_\parallel \parallel c$ |        |
| $F_1$               | 85                               | -2.0     | $\times$ | $\times$ | $\checkmark$ | $\times$ |
| $F_2$               | 79                               | 3.4      | $\times$ | $\times$ | $\checkmark$ | $\times$ |
| $F_3$               | 102                              | 2.7      | $\times$ | n.r.     | $\checkmark$ |        |
| $F_4$               | 119                              | 2.7      | n.r.     | n.r.     | $\checkmark$ |        |
| $F_5$               | 65                               | -0.6     | $\checkmark$ | $\times$ | $\times$ |        |
| $F_6$               | 83                               | -1.6     | $\checkmark$ | $\times$ | $\times$ |        |
| $F_7$               | 87                               | -1.7     | $\checkmark$ | $\times$ | $\times$ |        |
| $F_8$               | 91                               | -0.2     | $\checkmark$ | n.r. | $\times$ |        |
| $F_9$               | 102                              | 2.3      | $\checkmark$ | n.r. | $\times$ |        |
| $F_{10}$            | 76                               | -1.7     | $\times$ | $\checkmark$ | $\times$ |        |
| $F_{11}$            | 83                               | -1.9     | $\times$ | $\checkmark$ | $\times$ |        |
| $MM2 (y = 0)$       | 87                               | -2.0     | - | $\times$ | $\checkmark$ | $H_\omega \perp \perp c$ |
| $MM2, \nu_3 (y = 0.125)$ | 87                              | -2.5     | - | $\times$ | $\checkmark$ | $H_\omega \perp \perp c$ |
| $\nu_1 (y = 0.25)$ | 47                               | 4.0      | - | $\times$ | $\checkmark$ | $H_\omega \perp \perp c$ |
| $\nu_2 (y = 0.25)$ | 76                               | 2.6      | - | $\times$ | $\checkmark$ | $H_\omega \perp \perp c$ |
| $\nu_3 (y = 0.25)$ | 87                               | -2.6     | - | $\checkmark$ | $\checkmark$ | $E_\omega \perp \perp c$ |
| $\nu_1 (y = 0.4)$  | 47                               | 4.0      | - | $\checkmark$ | $\checkmark$ | $E_\omega \perp \perp c$ |
| $\nu_2 (y = 0.4)$  | 73                               | 3.6      | - | $\times$ | $\checkmark$ | $H_\omega \perp \perp c$ |
| $\nu_3 (y = 0.4)$  | 87                               | -3.1     | - | $\checkmark$ | $\checkmark$ | $E_\omega \perp \perp c$ |
| $\nu_4 (y = 0.5)$  | 42                               | -        | - | $\times$ | $\checkmark$ | $H_\omega \perp \perp c$ |

Corresponds to the number of excitation branches in the AFM phase below $H_{c1}$, if the $EM_1$ mode is assumed to be doubly degenerate and $M_5$ corresponds to a single mode. However, it is important to note that demagnetization factors due to the samples’ shapes can influence the observed eigenfrequency and field dependence of the modes in the FiM phase, making it difficult to relate the observed modes for different configurations and to conclude, whether some of them are actually equivalent. A direct comparison of the eigenfrequencies in zero-field and the effective g-factors is provided in Table II, together with the FiM modes previously reported for (Fe$_{1-y}$Zn$_y$)$_2$Mo$_3$O$_8$ 8-10. The corresponding effective g-factors of these modes were determined by us using the published data. Unfortunately, it is not possible to determine clear selection rules for the FiM modes, either because the excitations could not be resolved experimentally or their presence or absence in the three polarization configuration does not yield a consistent selection rule. For example, mode $F_1$ agrees well both in eigenfrequency and g-factor to the magnetic-dipole active mode $MM_2$ reported for $y = 0$ and $y = 0.125^8$, where the selection rule $H_\omega \perp \perp c$ was established by investigating an $ac$-cut sample in Voigt configuration, only. From our measurement in Voigt configuration alone, we would derive the same selection rule, but the absence of this mode in our $ab$-cut measurements with $H_\omega \perp \perp c$ does not allow to establish this selection rule. Similarly, modes $F_5 - F_9$ should appear in one of the configurations in the $ac$-cut measurements to establish a selection rule, but there seem to be no corresponding excitations.

In principle, the symmetry of the FiM phase was found to allow the occurrence of gyrotropic birefringence as reported for excitations $\nu_2$ and $\nu_3$ for Zn concentrations of $x = 0.25$ and $x = 0.4^9$, which seem to have no direct correspondence to the mode observed in this study. However, we can not exclude that similar magnetoelectric effects might be present for some of these modes.

Vibronic nature of the absorption band $V_1$

In the following we will analyze the nature of the electric-dipole active excitation band $V_1$, which emerges and gains intensity with decreasing temperatures below $T_N$ (see Fig. 6(b)). It can only be observed for $E_\omega \parallel a$ and does not exhibit any changes in magnetic fields up to 7 T. The onset of the excitation occurs at about 10 cm$^{-1}$, which is in agreement with the reported energy difference between the ground and first excited state of the Fe$^{2+}$ ions in tetrahedral environment for pure Fe$_2$Mo$_3$O$_8$ 17 and the proposed splittings of the lowest-lying states for both tetrahedral and octahedral sites 8.

The Jahn-Teller active Fe$^{2+}$ ions in tetrahedral environment are expected to couple to lattice vibrations, leading to vibronic excitations, where electronic and vi-
in the FiM state and (b) at $H = 2\,T$ in the AFM state for the three polarization configurations. The splitting of the AFM modes $M_1 - M_4$ is indicated in (b).

The number $n$ corresponds to the number of phonons involved in the absorption process, and, hence, the zero-phonon-line with $n = 0$ describes the purely electronic transition at $\omega_0$, which is not visible in our spectra.

In order to simulate the resulting vibrational lineshape we follow the approach by Rtsep et al.\(^\text{28}\), who use the empirical coupling function

$$s(\omega) = \exp\left(-\frac{\omega}{\omega_1}\right) \frac{\omega^2 S_1}{2\omega_1^3} + \exp\left(-\frac{\omega}{\omega_2}\right) \frac{\omega^3 S_2}{6\omega_2^4}$$

where the first term is motivated by a Debye-like phonon density of states with an exponential decay around the Debye frequency $\omega_1$, while the second term is an empirical modification of the phonon-density of states satisfying the condition $S = S_1 + S_2$.

In order to analyze the lineshape of the $V_1$ excitation, we use a spectrum obtained for $E^\perp c, H^\parallel c$ (ab-cut sample) and subtract the high-frequency contribution stemming from the lowest-lying infrared-active phonon modelled by a Lorentzian lineshape with eigen-frequency $\omega_p = 128.6\,\text{cm}^{-1}$, damping $\gamma = 9.0\,\text{cm}^{-1}$, and ionic plasma frequency $\omega_p = 158.4\,\text{cm}^{-1}$ (see Fig. 6(a)) in agreement with reported data for pure Fe$_2$Mo$_3$O$_8$.\(^\text{17}\) As the narrow electric-dipole excitation $EM_1$ on top of the $V_1$-band is suppressed in the ferrimagnetic phase above $H_{c2}$ (Fig. 4) and $M_4$ is clearly magnetic in origin, while $V_1$ does not alter, we do not consider any coupling of these excitations.

To restrict the parameters for this simulation, we fixed the zero-phonon-line to $\omega_0 = 12\,\text{cm}^{-1}$, a value close to experimental reports\(^\text{17}\) and theoretical estimates\(^\text{6}\) and minimized the number of phonons involved in the process to $n = 3$. Using these constraints, we could reproduce the experimental lineshape with the parameters $S_1 = 0.02$, $S_2 = 1.1$, $\omega_1 = 12\,\text{cm}^{-1}$, $\omega_2 = 3.6\,\text{cm}^{-1}$ and the amplitude $A = 2.4 \times 10^3\,\text{cm}^{-1}$, which is defined by $\alpha(\omega) = A \cdot I(\omega)$. The agreement between data and simulation is very good and, hence, we conclude that this simple approach satisfactorily reproduces the $V_1$ band and supports a vibronic origin of the band. Note, that
higher convolutions for \( n > 3 \) do only weakly modify the high-frequency tail, and the first Debye-like term of the coupling function alone does not allow to fully capture the entire absorption band. The values for \( \omega_1 \) and \( \omega_2 \) must be regarded as a parametrization of the acoustic phonon branches coupled to the electronic transitions. As such a vibronic band has not been reported for pure \( \text{Fe}_2\text{Mo}_3\text{O}_8 \), we assume that the disorder introduced by the Zn ions and the corresponding impurity modes are responsible for the occurrence of this vibronic band. It remains to be clarified why THz studies of samples with \( y > 0.1 \) do not report a similar vibronic feature\(^8\)–\(^{10}\) and why this vibronic mode is only present below \( T_N \). A possible reason for the emergence below \( T_N \) could be that the magnetic ordering triggers the splitting of the lowest-lying iron orbitals as suggested in Ref\(^6\).

V. SUMMARY

We observed ten magnetic modes in the AFM state in \( \text{Fe}_{1.8}\text{Zn}_{0.2}\text{Mo}_3\text{O}_8 \) in finite magnetic fields, including both magnetic- and electric-dipole active modes. Assuming that the lowest-lying mode is a doublet with an unresolved splitting in the magnetic fields applied in this study, the actual number of AFM modes would increase to eleven. This is the number of modes observed in the magnetic field induced FiM state in \( \text{Fe}_{1.8}\text{Zn}_{0.2}\text{Mo}_3\text{O}_8 \). The large number of modes, far exceeding the number of magnetic sublattices in pure \( \text{Fe}_2\text{Mo}_3\text{O}_8 \), may imply that the number of magnetic sublattices is increased due to Zn substitution on the tetrahedral sites. Another possible reason for the large number of excitations is that spin-stretching modes also become optically active, besides the precessional modes described by linear spin-wave theory. In the transition region between the two magnetic phases a coexistence of AFM and FiM modes is present, implying a coexistence of AFM and FiM phases for \( H_{c1} < H < H_{c2} \). Additionally, a broad electric-dipole active excitation band was observed in the AFM phase and identified to be of vibronic origin involving the lowest-lying electronic d-states of Fe in tetrahedral environment, which are split by about 12 \( \text{cm}^{-1} \).

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