Infrared-active phonon modes in monoclinic multiferroic MnWO$_4$

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We report on polarized infrared reflectivity measurements of multiferroic, monoclinic MnWO$_4$ between 10 K and 295 K. The full dielectric tensor and the frequency dependence of the orientation of the principal axes have been determined in the frequency range of the phonons. All infrared-active phonon modes (7 $A_u$ modes and 8 $B_u$ modes) are unambiguously identified. In particular the strongest $B_u$ modes have been overlooked in previous studies, in which the monoclinic symmetry was neglected in the analysis. Using a generalized Drude-Lorentz model, we determine the temperature dependence of the phonon parameters, including the orientation of the $B_u$ modes within the $ac$ plane. The phonon parameters and their temperature dependence have been discussed controversially in previous studies, which do not include a full polarization analysis. Our data does not confirm any of the anomalies reported above 20 K. However, in the paramagnetic phase we find a drastic reduction of the spectral weights of the weakest $A_u$ mode and of the weakest $B_u$ mode with increasing temperature. Below 20 K, the parameters of the $A_u$ phonon modes for $E \parallel b$ show only subtle changes, which demonstrate a finite but weak coupling between lattice dynamics and magnetism in MnWO$_4$. A quantitative comparison of our infrared data with the quasi-static dielectric constant $\varepsilon_{\parallel}$ indicates that the spectral weight of the electromagnon is tiny for $E \parallel b$, in particular much smaller than the weak changes of the spectral weight of the phonons.

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I. INTRODUCTION

The metal tungstate family AWO$_4$ with divalent A metal ions includes a number of compounds with interesting properties. The range of possible applications is very broad, including (phonon-) scintillation detectors, laser waveguides, laser crystals, and photocatalysis.$^{[1-6]}$ The compound MnWO$_4$, also known from nature as mineral hübnerite, belongs to the class of multiferroics, displaying a coexistence of antiferromagnetic and ferroelectric order parameters.$^{[7-9]}$ The Mn$^{2+}$ ions are in a high-spin 3d$^5$ configuration with spin $S = 5/2$. Magnetic frustration leads to a competition of magnetic ground states. Upon cooling, one finds a series of magnetic phase transitions$^{[9,10]}$ first to an incommensurate collinear antiferromagnetic phase (AF3) at $T_{N3} = 13.5$ K, then to an incommensurate spiral phase (AF2) at $T_{N2} = 12.5$ K, and finally at $T_{N1} \approx 6.5 – 8.0$ K to a commensurate collinear phase (AF1). A ferroelectric polarization and thus magnetoelectric multiferroicity is observed in the AF2 phase$^{[7,9]}$ as well as in a further phase occurring in high magnetic fields.$^{[11]}$ The spontaneous polarization is parallel to the $b$ axis.$^{[5]}$ Ferroelectricity originates from the spiral spin structure via the inverse Dzyaloshinskii-Moriya effect.$^{[7,12,13]}$ Recently, it was pointed out that also competing isotropic exchange interactions are important for multiferroicity.$^{[13]}$ The coupling between electric and magnetic effects gives rise to a particularly rich physics, ranging from the switching of the electric polarization by an external magnetic field$^{[14]}$ via the coupling of magnetic and electric domains$^{[15]}$ to second-harmonic generation from an incommensurate magnetic structure$^{[16]}$ and to a magnetoelectric memory effect.$^{[12,19]}$

The magnetoelectric coupling is not restricted to static properties but is also relevant for the dynamics. The character of magnons may change from purely magnetic to magnetoelectric, and these so called electromagnons

![FIG. 1: (Color online) Sketch of the crystal structure of monoclinic MnWO$_4$ highlighting the chains of WO$_6$ octahedra running along the $c$ axis. Left: $ac$ plane, right: $bc$ plane. Dark red spheres refer to the O(2) ions with short W-O(2) bonds of only 1.79 Å. The WO$_6$ octahedra are connected along edges via two O(1) ions (light red spheres). Within one octahedron, the diagonals are either formed by a short W-O(2) bond (thick, dark red lines) in combination with a long W-O(1) bond (2.13 Å, thin, yellow lines) or by two of the shorter W-O(1) bonds (1.91 Å, thin, light red lines). The two blue lines in the bottom left corner indicate the orientations of the two highest $B_u$ phonon modes as derived from the infrared reflectance data. The orientations of these two modes support the interpretation as W-O bond stretching modes.](arXiv:1406.6313v1 [cond-mat.str-el] 24 Jun 2014)
can be excited by the electric field component of an electromagnetic wave, i.e., electromagnons contribute to the optical conductivity and to the dielectric function $\varepsilon(\omega)$. The $f$-sum rule for the real part of the optical conductivity states that the total spectral weight is conserved, thus the spectral weight of the electromagnons has to be transferred from another dipole-active excitation. In the multiferroic phase of the manganites $\text{AMnO}_3$ (with $A = \text{Gd}_{1-x}\text{Tb}_x$ and $\text{Eu}_{1-x}\text{Y}_x$), the spectral weight of the electromagnons partially is taken away from the phonon mode lowest in energy. This behavior differs from the familiar case of proper ferroelectrics with a displacive phase transition. There, the continuous phase transition into the polar phase is accompanied by the softening of an infrared-active phonon mode. At the phase transition, the vanishing phonon frequency $\omega_p$ leads to a divergence of the static permittivity via a diverging contribution to the dielectric function (or oscillator strength) $\Delta\varepsilon \propto (\omega_p/\omega_0)^2$, where $\omega_0$ denotes the phonon plasma frequency. This does not require a change of the phonons spectral weight $\omega_p^2$ in the optical conductivity. Multiferroic $\text{MnWO}_4$ is an improper ferroelectric, in which ferroelectricity is not directly connected to a softening phonon but rather to the onset of complex magnetic order, i.e., to a softening of an electromagnon or of the related fluctuations as observed in dielectric spectroscopy with an electric field parallel to the $b$ axis. The concomitant reduction of the symmetry yields a finite spectral weight for electromagnons. A detailed study of the lattice vibrations and of the phonon parameters thus may provide valuable information about the ferroelectric transition and the spin-lattice coupling.

In monoclinic $\text{MnWO}_4$, several results suggest that the spin-lattice coupling is only weak. High-resolution thermal expansion data show only subtle but clear anomalies at both $T_{N1}$ and $T_{N3}$. The ferroelectric polarization is of the order of $50 \mu C/m^2$ more than an order of magnitude smaller than in, e.g., $\text{TbMnO}_3$. At $T_{N1}$, the static dielectric constant along the $b$ axis, $\varepsilon_b$, shows only a small jump of roughly $0.01$ which is about two orders of magnitude smaller than the effects observed in the manganites at low frequencies. The phonon modes have been studied by Raman scattering and optical spectroscopy. Using polarized Raman scattering, Ilev et al. found no anomalies of the phonon parameters down to 5 K, while Dura et al. reported an enhanced damping of several phonon modes in the ferroelectric AF2 phase which was attributed to spin-phonon interactions. In contrast, Hoang et al. observed phonon anomalies at about 50 K and between 150 and 200 K in their Raman data of $\text{MnWO}_4$ and suggested a new phase transition at 180 K, far above the known magnetic phase-transition temperatures. As far as the infrared-active phonon modes are concerned, a consistent description has not been obtained yet. Choi et al. measured polarized reflectivity spectra and found no anomalies as a function of temperature. However, the reflectivity was investigated only for 3 different polarization directions of the electric field $E$ ($E \parallel a$, $b$, and $c$), which is not sufficient for this monoclinic compound where $a$ and $c$ are not perpendicular to each other.

Remarkably, stronger anomalies were reported both in Raman and infrared data for polycrystalline samples of $\text{Mn}_{1-x}\text{A}_x\text{WO}_4$ doped with a few percent of $A = \text{Fe}$, $\text{Co}$, or $\text{Ni}$ Most of these anomalies are observed between 20 K and 200 K, i.e., far above the magnetic phase-transition temperatures of undoped $\text{MnWO}_4$. In the case of $A = \text{Co}$, high-resolution synchrotron X-ray diffraction data for $x = 0.05$ and 0.20 show only small anomalies at the magnetic phase transitions. Moreover, the reported eigenfrequencies of the slightly doped samples strongly deviate from those reported for pure $\text{MnWO}_4$. None of these studies takes the monoclinic structure fully into account. For monoclinic symmetry, the character of optical phonon modes in general is a mixture of transverse (TO) and longitudinal (LO), and this mixture depends on the direction of the wavevector $k$. Due to the LO-TO splitting, also the eigenfrequency of a given phonon mode depends on the direction of $k$, thus the apparent peak frequency depends on the experimental geometry. This explains the difficulties in determining even the correct eigenfrequencies, in particular for polycrystalline samples. To the best of our knowledge, an analysis of the full dielectric tensor in the frequency range of the phonons has not been reported for any monoclinic tungstate $\text{AWO}_4$ with divalent A metal ions thus far.

Further infrared studies were performed on nanocrystalline $\text{MnWO}_4$ with different morphology of the nanoparticles. In contrast to Raman modes, the infrared-active phonons show a pronounced dependence on particle size and morphology. As stated above, this is in fact not surprising since the TO-LO mixture and thus the mode frequency depend on the direction of $k$. It has been concluded that a detailed understanding of the bulk modes is a prerequisite to understand the phonon modes of nanocrystals.

Here, we report on a full polarization analysis of single crystalline $\text{MnWO}_4$, which allows us to identify unambiguously all expected phonon modes, both for $A_u$ and $B_u$ symmetry. Using a generalized Drude-Lorentz model, we determine the temperature dependence of all phonon parameters, including the orientation of the $B_u$ modes within the $ac$ plane. Comparison with previous studies shows that in particular the strongest modes have been overlooked thus far. This surprising result can be explained easily. Weaker modes show a small LO-TO splitting and thus give rise to rather narrow but clear features. Strong modes with a very large LO-TO splitting yield broad features, and the orientational dispersion of the dielectric tensor gives rise to unusual line shapes of these broad peaks. Moreover, the TO-LO mixture depends on the direction of the wavevector $k$ and thus the eigenfrequency of modes with a large LO-TO splitting may change strongly as a function of $k$. 
II. EXPERIMENTAL

Single crystals of MnWO$_4$ were grown from the melt using the top-seeding technique. The Mn ions can be kept in the divalent state during growth by using a high growth temperature and avoiding melt solvents. We obtained ruby-red transparent crystals with dimensions up to $5 \times 5 \times 25$ mm$^3$. The crystal structure of MnWO$_4$ is monoclinic with space group $P2_1/c$, the monoclinic angle amounts to $\beta = 91.08^\circ$. Edge-sharing distorted [MnO$_6$] octahedra and edge-sharing distorted [WO$_3$] octahedra form alternating zig-zag chains running along the c axis, see Fig. 1. We used natural growth faces and Laue diffraction for the crystallographic sample orientation.

After orientation, the samples were lapped and polished.

Using a Bruker IFS 66v/S Fourier-transform spectrometer, we performed reflectivity measurements at nine different temperatures ranging from 10 K to 295 K in the frequency range of 50 - 7000 cm$^{-1}$. The sample was mounted on the cold finger of a continuous-flow He cryostat. The angle of incidence $\alpha$ was about 11$^\circ$, i.e., near-normal incidence. The incident light was linearly polarized, while the polarization state of the reflected light was not analyzed. The temperature of the sample was measured with a thermometer glued on the sample, avoiding a direct thermal contact between thermometer and sample holder. We report data down to 20 K for the paramagnetic phase, for 13 K in the AF3 phase, and for 10 K in the multiferroic AF2 phase. The phase transition to the magnetic phase, for 13 K in the AF3 phase, and for 10 K in the AF2 phase. The sample surface deviates by 10$^\circ$ from a (100) surface, i.e., $\varphi = 80^\circ$ denotes the angle by which the x axis has to be rotated around the y axis to coincide with the sample surface. In the same geometry, we measured the reflectivity $R_p(\omega, \alpha, \varphi)$ for p-polarized light, i.e., with $E \parallel b$.

For a full polarization analysis of this monoclinic compound, we measured the reflectivity $R_{ac}(\omega, \chi)$ on a (010) surface, where $\chi$ denotes the angle between the incident electric field $E \parallel b$ and the x axis, see Fig. 2). For simplicity, we assume normal incidence for the definition of $\chi$ and for the analysis of $R_{ac}(\omega, \chi)$. The polarization direction $\chi$ was varied by rotating not the sample but the polarizer using a stepper motor. This bears the advantages that the angular precision is higher and that the polarization angle can be changed while the sample is kept at low temperature. The disadvantage is that the incident electric field is not exactly parallel to the ac plane (with the exception of s-polarized light) due to the finite angle of incidence. We measured $R_{ac}(\omega, \chi)$ for $\chi = 0^\circ$, $30^\circ$, $60^\circ$, and $90^\circ$, see Fig. 3. Any three of these data sets can be used to calculate $R_{ac}(\omega, \chi)$ for any value of $\chi$. The comparison of the measured reflectivity for $\chi = 60^\circ$ with the calculated one in Fig. 4 demonstrates the consistency of our data.

Additionally, we measured the real part of the quasi-static dielectric constant along the $b$ axis, $\text{Re}(\varepsilon_b)$, between 5 K and 50 K at 96.8 kHz and 45 MHz. At 96.8 kHz we employed a frequency-response analyzer (NOVOCONTROL) and a small single crystal of MnWO$_4$ with dimensions of about $2 \times 0.5 \times 2$ mm$^3$ which was prepared as plate-type capacitor using silver-paint electrodes on the
The number of phonon modes can be derived from a factor-group analysis. Monoclinic MnWO$_4$ with space group $P2/c$ has $Z = 2$ formula units per unit cell. For $T = 295$ K, the site symmetries as well as the irreducible representations of each atomic site are given in Tab. I. In the presence of a center of inversion, Raman activity and infrared activity of normal modes are mutually exclusive. In total the irreducible representations contain 36 modes,

$$\Gamma_{\text{total}} = 8 A_g + 8 A_u + 10 B_g + 10 B_u.$$  

(1)

Subtracting the acoustic modes ($A_u + 2 B_u$) and the Raman modes ($8 A_g + 10 B_g$), we find 15 infrared-active phonon modes

$$\Gamma_{\text{IR}} = 7 A_u + 8 B_u.$$  

(2)

The factor-group analysis thus predicts seven $A_u$ modes for polarization of the electric field $E \parallel b$ and eight $B_u$ modes for polarization within the $ac$ plane, $E \perp b$. The magnetic phase transition at $T_{N3}$ is not connected with a structural phase transition, thus our analysis is valid down to $T_{N2} = 12.5$ K. Below $T_{N2}$, the appearance of ferroelectricity reflects the loss of a mirror plane and a concurrent change of the selection rules. A distinction between Raman-active and infrared-active modes is not strictly valid anymore. However, the ferroelectric polarization $P_b$ is only small in MnWO$_4$, about 50 $\mu$C/m$^2$. Thus the ionic displacements $\delta u \propto P_b$ are expected to be small, they have escaped detection in structural studies thus far. Accordingly, we expect that the Raman-active modes acquire only a tiny spectral weight $\Delta \varepsilon \propto P_b^2$ in the dielectric function below $T_{N2}$, possibly below the detection limit.

### TABLE I: Atomic site symmetries and irreducible representations for the atoms in monoclinic MnWO$_4$ with space group $P2/c$.

| Wyckoff site | irreducible atom notation symmetry | representations |
|--------------|-----------------------------------|-----------------|
| Mn           | 2(f) C2                           | $A_g + A_u + 2B_g + 2B_u$ |
| W            | 2(e) C2                           | $A_g + A_u + 2B_g + 2B_u$ |
| O(1)         | 4(g) C1                           | $3A_g + 3A_u + 3B_g + 3B_u$ |
| O(2)         | 4(g) C1                           | $3A_g + 3A_u + 3B_g + 3B_u$ |

FIG. 4: (Color online) Solid: measured reflectivity $R_{ac}(\omega, \chi)$ for $\chi = 60^\circ$ at $T = 10$ K. Red dashed: calculated reflectivity $R_{ac}^{\text{cal}}(60^\circ) = -\frac{1}{2} R_{ac}(0^\circ) + R_{ac}(30^\circ) + \frac{1}{2} R_{ac}(90^\circ)$. The maximum deviation between measured and calculated data amounts to $5\%$ at about 600 cm$^{-1}$.

### IV. DIELECTRIC RESPONSE OF A MONOCLINIC COMPOUND

In monoclinic MnWO$_4$, the tensor of the dielectric function $\varepsilon(\omega)$ has the following form:

$$\varepsilon(\omega) = \begin{pmatrix} \varepsilon_{xx}(\omega) & \varepsilon_{xz}(\omega) & 0 \\ \varepsilon_{xz}(\omega) & \varepsilon_{yy}(\omega) & 0 \\ 0 & 0 & \varepsilon_{zz}(\omega) \end{pmatrix}.$$  

(3)

Here, we used the Cartesian coordinate system defined in Sec. II with $y \parallel b, z \parallel c$, and $x$ lying in the ac plane (see Fig. 2). Without external magnetic field and neglecting a possible magnetization, the off-diagonal matrix elements $\varepsilon_{xz}$ and $\varepsilon_{yy}$ are identical. We decompose the three-dimensional tensor $\varepsilon(\omega)$ into a scalar $\varepsilon_b(\omega) = \varepsilon_{yy}(\omega)$ and a two-dimensional tensor

$$\varepsilon_{ac}(\omega) = \begin{pmatrix} \varepsilon_{xx}(\omega) & \varepsilon_{xz}(\omega) \\ \varepsilon_{xz}(\omega) & \varepsilon_{zz}(\omega) \end{pmatrix}.$$  

(4)

The scalar $\varepsilon_b(\omega)$ contains information on the $A_u$ modes and can be studied by measuring the reflectivity $R_b(\omega)$ with $E \parallel b$ and a subsequent analysis using a Drude-Lorentz model (see Sec. IV A). For the analysis of $\varepsilon_{ac}(\omega)$ and the modes with $B_u$ symmetry, we employed three different methods: a generalized Drude-Lorentz model (see Sec. IV A), an oscillator model which allows for an asymmetric (non-Lorentzian) line shape (see Sec. IV B), and a Kramers-Kronig-constrained variational analysis (KKvar, see Sec. IV D). The two-dimensional tensor $\varepsilon_{ac}(\omega)$ can be determined by measuring the reflectivity $R_{ac}(\omega, \chi)$ with $E \perp b$ for three different polarization directions $\chi$ (see Sec. II and Fig. 2). For the analysis of $R_{ac}(\omega, \chi)$, we assume normal incidence and that the incident wave excites only transverse modes. For $E \perp b$, the excitation of purely transverse modes actually requires that $k \parallel b$, i.e., strictly normal incidence on a (010) plane. A posteriori, this assumption of purely transverse excitations is validated by our analysis with the exception of the $B_u$ mode highest in energy, which is nearly degenerate with a longitudinal mode and shows a non-Lorentzian
line shape (see Sec. V C). We use the terms transverse mode and longitudinal mode for, e.g., the discussion of a strong Reststrahlen band (with reflectance close to 1) in $R_{ac}(\omega, \chi)$, even though a strict distinction between TO and LO modes is not valid in general for monoclinic symmetry.

A. Generalized Drude-Lorentz model

To determine the scalar $\varepsilon_b(\omega)$ from the measured reflectivity data in the frequency domain of the phonon modes, $\varepsilon_b(\omega)$ can be described by a sum of oscillators. We employ a Drude-Lorentz model

$$\varepsilon_b(\omega) = \varepsilon_b^\infty + \sum_{i,A} \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i \omega},$$

where $\varepsilon_b^\infty$ denotes the high-frequency dielectric constant, $\omega_{0,i}$ the transverse eigenfrequency, $\omega_{p,i}$ the plasma frequency, and $\gamma_i$ the damping of the $i$-th oscillator, where $i$ is running over all $A_n$ modes. The oscillator strength is given by $\Delta\varepsilon_i = (\omega_{p,i}/\omega_{0,i})^2$.

Parametrization of $\tilde{\varepsilon}_{ac}(\omega)$ is somewhat more difficult because the axes $a$ and $c$ are not perpendicular to each other. For any frequency, one can find a set of orthogonal axes within the $ac$ plane such that the real part of $\tilde{\varepsilon}_{ac}$ has diagonal form and a second set of axes for which the imaginary part is diagonal. In case of a monoclinic MnWO₄, symmetry fixes only the $y$ axis of the tensor $\tilde{\varepsilon}$ with respect to the crystallographic axes, the two other axes may rotate within the $ac$ plane. The rotation angles $\phi_{ac}(\omega)$ and $\phi_{ba}(\omega)$ of the principal axes of Re$\{\tilde{\varepsilon}_{ac}(\omega)\}$ and Im$\{\tilde{\varepsilon}_{ac}(\omega)\}$ may differ from each other and depend on the frequency $\omega$. This orientation of the transverse axes of the dielectric tensor usually gives rise to the so-called axial dispersion, i.e., an orientational dispersion of the optical axes. For a given frequency $\omega_0$, $\phi_{ac}(\omega_0) \neq \phi_{ba}(\omega_0)$ implies that the complex tensor $\tilde{\varepsilon}_{ac}(\omega)$ cannot be diagonalized by a rotation. In terms of an oscillator model, the orientational dispersion of $\tilde{\varepsilon}_{ac}(\omega)$ can be described by assigning a particular orientation to each oscillator. This generalized Drude-Lorentz (gDL) model reads

$$\tilde{\varepsilon}_{ac}^{DL}(\omega) = \varepsilon_{ac}^\infty + \sum_{i,B_n} \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i \omega} \times S(\theta_i) \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} S^{-1}(\theta_i),$$

where $\varepsilon_{ac}^\infty$ is a symmetric real two-dimensional tensor denoting the high-frequency contribution, $\theta_i$ is the angle by which the dipole moment of mode $i$ has to be rotated to coincide with the $x$ axis, and $S(\theta_i)$ is the rotation matrix

$$S(\theta_i) = \begin{pmatrix} \cos \theta_i & -\sin \theta_i \\ \sin \theta_i & \cos \theta_i \end{pmatrix}.$$  

Note that $\theta_i$ and $\phi_{ac}(\omega_0,i)$ or $\phi_{ba}(\omega_0,i)$ do not have to coincide. In case of a weak mode, $\phi_{ac}(\omega_0,i)$ may be dominated by a stronger mode which is close in energy, and thus $\theta_i$ and $\phi_{ac}(\omega_0,i)$ may differ significantly from each other.

B. Asymmetric oscillator model

On the whole, the generalized Drude-Lorentz model yields a satisfactory description of the reflectance of MnWO₄. However, the highest $B_n$ phonon mode shows an unusual line shape in $R_{ac}(\omega, \chi)$ (see Sec. V C). In case of a scalar dielectric function, an asymmetric line shape [or, more precisely, a non-Lorentzian line shape of $\varepsilon(\omega)$] can be described using a factorized four-parameter model which employs two different values $\gamma_{L,i}$ and $\gamma_{T,i}$ for the damping of the $i$-th oscillator at the transverse and longitudinal eigenfrequencies. This mimics an approximately quadratic frequency dependence of the damping $\gamma = \gamma(\omega)$. However, the condition $\gamma_{L,i} > \gamma_{T,i}$ has to be satisfied thus the factorized model is capable of describing an asymmetric mode which is steep at low frequencies and washed out at the high-frequency side. Our data show the opposite behavior (see below). Moreover, the factorized model describes a scalar dielectric function and cannot be written as a sum of individual oscillators, thus the generalization of the factorized model for monoclinic symmetry with orientational dispersion of $\tilde{\varepsilon}_{ac}(\omega)$ is not straightforward.

For the description of a non-Lorentzian line shape in the tensor $\tilde{\varepsilon}_{ac}(\omega)$, we choose a different approach starting from a sum of oscillators, as described in Eq. (9). A thorough discussion of the frequency dependence of the damping $\gamma(\omega)$ requires to treat $\gamma(\omega)$ as a response function in order to keep $\tilde{\varepsilon}_{ac}(\omega)$ Kramers-Kronig consistent, i.e., to obey causality. To this end, we consider the coupling between two oscillators as discussed by Barker and Hopfield (a simplified version valid in a narrow frequency range has been proposed by Humlíček et al.). More precisely, we study the coupling of one infrared-active mode (IR) and one IR-silent mode (s) with vanishing effective charge in order to describe the unusual line shape of the highest $B_n$ mode. A possible candidate for the IR-silent mode is a Raman-active mode. In MnWO₄, we find the highest $B_n$ mode at 767 cm⁻¹ at 10 K which is close in energy to the highest $B_2$ mode observed at 776 cm⁻¹ at 5 K. Another possible origin of the asymmetric line shape is the mixing between transverse and longitudinal modes, see Sec. V C. However, we may also adopt a phenomenological point of view, in which case we do not have to identify this silent mode with a particular eigenmode of the compound but view it as a phe-
momentological source for an asymmetric line shape of the infrared-active mode. The dielectric function can be derived from the classical equations of motion for two damped harmonic oscillators with eigenfrequencies $\omega_{\text{IR}}$ and $\omega_s$ and damping constants $\gamma_{\text{IR}}$ and $\gamma_s$, respectively,

$$
\ddot{x}_{\text{IR}} = -\omega_{\text{IR}}^2 x_{\text{IR}} - \omega_{\text{IR}}^2 s_{\text{IR}} (x_{\text{IR}} - x_s) - \gamma_{\text{IR}} \dot{x}_{\text{IR}} + \frac{e E_0}{m} e^{-i\omega t} \\
\ddot{x}_s = -\omega_s^2 x_s - \omega_{\text{IR}}^2 s_{\text{IR}} (x_s - x_{\text{IR}}) - \gamma_s \dot{x}_s
$$

(8)

where $x_i$ denotes the displacement of oscillator $i \in \{\text{IR}, s\}$, $t$ is the time, $E_0$ the amplitude of the driving electric field, $e$ and $m$ are the effective charge and mass of oscillator “IR”, and $s_{\text{IR}}$ describes the coupling. We are only interested in solutions for the polarization $P$ which oscillate with the frequency $\omega$ of the driving force,

$$
P = \varepsilon_0 [\varepsilon(\omega) - 1] E_0 e^{-i\omega t} = \frac{N}{V} e \varepsilon_{\text{IR}}
$$

(9)

with the density $N/V$ and the vacuum permittivity $\varepsilon_0$. Thus the dielectric function reads

$$
\varepsilon(\omega) = 1 + \frac{\omega_{\text{IR}}^2}{\omega_{\text{IR}}^2 + \omega_{\text{IR}}^2 s_{\text{IR}} - \omega^2 - i\gamma_{\text{IR}} \omega - \frac{\omega_{\text{IR}}^2}{\omega_{\text{IR}}^2 + \omega_{\text{IR}}^2 s_{\text{IR}} - \omega^2 - i\gamma_{\text{IR}} \omega}}
$$

(10)

with the plasma frequency

$$
\omega_{\text{p,IR}}^2 = \frac{1}{\varepsilon_0} \frac{N}{V} \varepsilon_e^2 m .
$$

(11)

Equation (10) reduces to the conventional Drude-Lorentz model (cf. Eq. [5]) for $\omega_{\text{IR}} = 0$. For finite $\omega_{\text{IR}}$, the damping is not a real function of $\omega$ but effectively is described by a complex term. The main merit of this model is that it offers a Kramers-Kronig-consistent way for the description of a non-Lorentzian line shape, which requires the introduction of three additional parameters ($\omega_s$, $\gamma_s$, and the coupling $\omega_{\text{IR}}s$). Here, we use this asymmetric model only for the $B_6$ phonon mode with the highest eigenfrequency. The total dielectric function thus reads

$$
\tilde{\varepsilon}_{\text{asym}}(\omega) = \varepsilon_{\text{asym}}^\infty + \sum_{i=1}^{7} \frac{\omega_{\text{p},i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i \omega} \\
\times S(\theta_i) \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} S^{-1}(\theta_i) \\
+ \frac{\omega_{\text{p},8}^2}{\omega_{0,8}^2 - \omega^2 - i\gamma_8 \omega - \frac{\omega_{\text{IR}}^2}{\omega_{\text{IR}}^2 + \omega_{\text{IR}}^2 s_{\text{IR}} - \omega^2 - i\gamma_{\text{IR}} \omega}} \\
\times S(\theta_8) \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} S^{-1}(\theta_8),
$$

(12)

with the abbreviations $\omega_{0,8}^2 := \omega_{\text{IR}}^2 + \omega_{\text{IR}}^2 s_{\text{IR}}$ and $\omega_{0,8}^2 := \omega_s^2 + \omega_{\text{IR}}^2 s_{\text{IR}}$.

### C. Reflectance and Fitting Procedure

For (near-)normal incidence, the reflectance $R_b(\omega)$ for $E \parallel b$ is given by

$$
R_b(\omega) = \left| \frac{1 - \sqrt{\varepsilon_{\text{IR}}(\omega)}}{1 + \sqrt{\varepsilon_{\text{IR}}(\omega)}} \right|^2 .
$$

(13)

whereas the reflectance $R_{ac}(\omega, \chi)$ is related to the tensor $\varepsilon_{ac}(\omega, \chi)$ via

$$
R_{ac}(\omega, \chi) = \left| \left( \left[ 1 - \sqrt{\varepsilon_{ac}(\omega)} \right] \cdot \left[ 1 + \sqrt{\varepsilon_{ac}(\omega)} \right] \right)^{-1} \right| \\
\times \left( \cos \chi \right)^2 ,
$$

(14)

where $\mathbf{I}$ and $(\ldots)^{-1}$ denote the unity tensor and the inverse tensor, respectively. The square root of the tensor $\varepsilon_{ac}(\omega)$ is taken by rotating $\varepsilon_{ac}(\omega)$ to a diagonal form (employing a “rotation” matrix with complex entries), then taking the square root for each matrix element, and the resulting matrix is rotated back to its original basis.

The reflectivity $R_p(\omega, \alpha, \varphi)$ measured for $p$-polarized light with (010) as plane of incidence [see Sec. II and Fig. 2a)] is given by

$$
R_p(\omega, \alpha, \varphi) = \frac{C \cos(\alpha) - \sqrt{\varepsilon_{uw}(\omega) - \sin^2(\alpha)}}{C \cos(\alpha) + \sqrt{\varepsilon_{uw}(\omega) - \sin^2(\alpha)}}^2
$$

(15)

with $C = \sqrt{\varepsilon_{uw}(\omega) - \varepsilon_{uw}^2(\omega)}$,

(16)

where $\alpha = 11^\circ$ denotes the angle of incidence. Here, we use a Cartesian coordinate system $u, v, w$ with $v \parallel b$ and $w$ normal to the surface, and $\varphi$ denotes the angle between the $x$ axis (which is fixed to the crystal axes) and the $u$ axis, i.e., the surface, see Fig. 2a). In our case, $\varphi = 80^\circ$. In the basis $u, w$, the tensor $\varepsilon_{ac}(\omega)$ is given by

$$
\begin{pmatrix} \varepsilon_{uw} & \varepsilon_{uw} \\ \varepsilon_{uw} & \varepsilon_{uw} \end{pmatrix} = \varepsilon_{uw}(\varphi, \omega) = S(\varphi) \varepsilon_{ac}(\omega) S^{-1}(\varphi),
$$

(17)

with the rotation matrix $S(\varphi)$ as described in Eq. 7. For $E \perp b$, the parameters of the generalized Drude-Lorentz model and of the asymmetric oscillator model were obtained by fitting the measured reflectance $R_{ac}(\omega, \chi)$ and $R_p(\omega, \alpha, \varphi)$ simultaneously. In $R_p(\omega, 11^\circ, 80^\circ)$, transverse and longitudinal modes are strongly mixed. The consideration of $R_p(\omega, 11^\circ, 80^\circ)$ thus offers an excellent test for the validity of the analysis, see Sec. V C.

For the fits we employed the MAGIX package (Modeling and Analysis Generic Interface for eXternal numerical codes), which allows to combine different optimization algorithms to make use of their specific advantages. One
may, e.g., combine a swarm algorithm to roughly localize a minimum in parameter space with the Levenberg-Marquardt algorithm to optimize the parameters. Due to the large number of parameters, we typically used only the Levenberg-Marquardt algorithm. However, we employed the particle-swarm-optimization algorithm and the interval-nested-sampling algorithm\cite{61} to search for alternative parameter values of weak oscillators.

D. Kramers-Kronig-constrained variational approach

In case of a scalar dielectric function such as $\varepsilon_b(\omega)$, a Kramers-Kronig analysis of, e.g., the normal-incidence reflectance $R_b(\omega)$ – with appropriate extrapolations to $\omega = 0$ and $\infty$ – allows for a model-independent determination of $\varepsilon_b(\omega)$. An extension to monoclinic symmetry has been discussed by Kuzmenko et al.\cite{52} Their approach still is based on a Kramers-Kronig analysis of the measured reflectance data [in this case $R_{ac}(\omega, \chi)$] but employs a variational analysis. More recently, a Kramers-Kronig-constrained generalization of the variational approach (KKVvar) has been discussed by Kuzmenko et al.\cite{53} In short, it uses a large number $N$ of oscillators, where $N$ is comparable to the number of measured data points. The $N$ eigenfrequencies $\omega_1, \ldots, \omega_N$ may, e.g., coincide with the frequency points of the measured data. The consistent width of each oscillator is of the order of the step size $\omega_{i+1} - \omega_i$, thus the contribution of any oscillator to the imaginary part $\text{Im}\{\varepsilon_{\text{KKvar}}(\omega)\}$ is restricted to a small frequency interval. The oscillator strengths of the $N$ oscillators are used to parameterize the frequency dependence of $\text{Im}\{\varepsilon_{\text{KKvar}}(\omega)\}$, whereas the real part $\text{Re}\{\varepsilon_{\text{KKvar}}(\omega)\}$ is obtained via a Kramers-Kronig transformation. Finally, the oscillator strengths are varied by fitting the experimental data. Due to the large number of oscillators, this approach is well suited to describe, e.g., asymmetric non-Lorentzian line shapes of phonon modes or tiny spectral details and still yields a Kramers-Kronig-consistent result for the dielectric function.

Here, we use $3N$ oscillators with a triangular profile\cite{52} at $N$ frequency points to parameterize $\text{Im}\{\varepsilon_{xx}^{\text{KKvar}}(\omega)\}$, $\text{Im}\{\varepsilon_{xx}^{\text{KKvar}}(\omega)\}$, and $\text{Im}\{\varepsilon_{zz}^{\text{KKvar}}(\omega)\}$. In order to reduce the calculational effort, we use a step size of 1 cm$^{-1}$ with $\omega_1 = 100$ cm$^{-1}$ and $\omega_N = 1000$ cm$^{-1}$. A Kramers-Kronig analysis requires a reasonable extrapolation beyond the underlying frequency mesh $\omega_1$ to $\omega_N$. Therefore, the result $\varepsilon_{\text{DL}}$ of the generalized Drude-Lorentz fit (cf. Eq. 6) is used as a starting point. The total dielectric function reads

$$\varepsilon_{\text{ac}}(\omega) = \varepsilon_{\text{DL}}(\omega) + \varepsilon_{\text{KKvar}}(\omega). \quad (18)$$

The signs of $\text{Im}\{\varepsilon_{xx}^{\text{KKvar}}(\omega)\}$, $\text{Im}\{\varepsilon_{xx}^{\text{KKvar}}(\omega)\}$, and $\text{Im}\{\varepsilon_{zz}^{\text{KKvar}}(\omega)\}$ are arbitrary with the constraints $\text{Im}\{\varepsilon_{xx}^{\text{total}}(\omega)\} \geq 0$ and $\text{Im}\{\varepsilon_{zz}^{\text{total}}(\omega)\} \geq 0$. We use this Kramers-Kronig-constrained variational approach to fit the reflectivity $R_{ac}(\omega, \chi)$ for three different polarization angles ($\chi = 0^\circ$, $30^\circ$, and $90^\circ$).

V. PHONON MODES

Figures 5 and 6 show the reflectance $R_{ac}(\omega, \chi)$ for three different polarization angles $\chi$ as well as $R_p(\omega, \alpha, \varphi)$ and $R_b(\omega)$ at $T = 10$ K and 295 K, respectively. Additionally, we show the reflectance as obtained from the fits based on the generalized Drude-Lorentz model. We fitted $R_p(\omega, \alpha, \varphi)$ and $R_{ac}(\omega, \chi)$ for $\chi \in \{0^\circ, 30^\circ, 90^\circ\}$ simultaneously. The fit parameters are listed in Tab. II. The asymmetric non-Lorentzian line shape observed in $R_{ac}(\omega, \chi)$ in case of the $B_u$ mode highest in energy is discussed in Sec. V C. In Sec. V D we address the temperature dependence of the spectra which is depicted in Fig. 7 for the range of low frequencies.

A. $A_u$ phonon modes

For $E \parallel b$, the agreement between data and fit is excellent, and the analysis is straightforward (see bottom panels of Figs. 5 and 6). The spectra show seven $A_u$ modes, in agreement with the predictions of the factor-group analysis for $T > T_{N2} = 12.5$ K. We do not find any additional mode at 10 K, i.e., below $T_{N2}$. The small discrepancies between data and fit around some of the maxima and minima of $R_b(\omega)$ can be attributed to small deviations from a Lorentzian line shape, typically caused by small contributions stemming from the multi-phonon continuum. Remarkably, the frequency of the highest $A_u$ mode amounts to 859 cm$^{-1}$, which is unusually high for a transition-metal oxide in which oxygen is the only light element. However, comparable values have been reported for other tungstates $A(WO_4)$ with divalent $A = \text{Cd}$, Ni, or Mg\cite{53,67}. This mode can be assigned to a symmetric W-O(2) bond stretching phonon. The high frequency reflects the strong bonding between the nominally hexavalent W ions and the O(2) ions, the shortest W-O(2) bond in $\text{MnWO}_4$ amounts to only 1.79 ˚A (see Fig. 1).\cite{57} Similar energies of stretching modes have been observed in, e.g., multiferroic $\text{Ni}_3\text{V}_2\text{O}_8$ and $\alpha'$-$\text{NaV}_2\text{O}_5$ with nominally penta- and tetravalent V ions.\cite{71} The character of the other $A_u$ modes is given in Tab. II.

As far as the eigenfrequencies $\omega_{0,i}$ of $A_u$ modes along the unique $b$ axis are concerned, the results of Refs. 10 and our data agree very well with each other. With the exception of the lowest $A_u$ mode, the values for $\omega_{0,i}$ agree within about 1.2%. In $\text{MnWO}_4$, we and Choi et al.\cite{40} find the lowest mode at 168 cm$^{-1}$ at room temperature, whereas it is reported at 180 and 182 cm$^{-1}$ in $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ and $\text{Mn}_{0.97}\text{Fe}_{0.03}\text{WO}_4$, respectively.\cite{41} Note that the values of the damping $\gamma_i$ and the oscillator strength $\Delta\varepsilon_i$ are not reported for the single crystal data in Refs. 10 and 41.
The shape of the electrodes. Note that impedance measurements typically result in data measured below the electromagnon eigenfrequency range. Combining this result with low-frequency data measured below the electromagnon eigenfrequency, the oscillator function, the parameters $\theta$ and $\omega_c$, can be identified. The longitudinal eigenfrequency is given in Ref. [41], $\omega_c = 6.25 (5.88)$, $\omega_c = 123(241)$ cm$^{-1}$, and $\omega_c = 283$ cm$^{-1}$. The mode with $\omega_c = 273$ cm$^{-1}$ has a larger oscillator strength, giving rise to the pronounced Reststrahlen band observed between about 250 cm$^{-1}$ and 400 cm$^{-1}$ for $\chi = 90^\circ$. The eigfrequencies can be read off more easily from $R_{ac}(\omega, \chi)$. Five of the eigfrequencies can be easily recognized in the data of $R_{ac}(\omega, \chi)$. Four out of these five modes can be easily recognized in the spectrum of $R_{ac}(\omega)$ for $\chi = 90^\circ$ below 300 cm$^{-1}$ at $T = 10$ K (see Fig. 7). These four modes have the eigfrequencies $\omega_{0,1} = 139$ cm$^{-1}$, $\omega_{0,2} = 201$ cm$^{-1}$, $\omega_{0,3} = 241$ cm$^{-1}$, and $\omega_{0,5} = 283$ cm$^{-1}$. The mode with $\omega_{0,4} = 273$ cm$^{-1}$ has a much larger oscillator strength.

The $A_u$ phonon parameters allow us to determine the contribution $\text{Re}\{\varepsilon_{b}^{\text{high}}\} = \varepsilon_{\infty} + \sum_{i=1}^{7}\Delta\varepsilon_i$ of phonons and of excitations at higher energies to the quasi-static dielectric constant $\text{Re}\{\varepsilon_b\}$, i.e., for frequencies well below the phonon range. Combining this result with low-frequency data measured below the electromagnon eigenfrequency allows us to estimate the contribution of the electromagnon to $\text{Re}\{\varepsilon_b\}$, which will be discussed together with the temperature dependence in Sec. [V D]. At 10 K we find $\text{Re}\{\varepsilon_{b}^{\text{high}}\} = 14.9$. This has to be compared with the results reported from impedance measurements using LCR meters, $\text{Re}\{\varepsilon_b\} = 16.4$ at 1 MHz (Ref. [1]) and 12.3 at 1 kHz (Ref. [8]). Note that impedance measurements typically show a high relative accuracy but larger errors concerning the absolute value due to uncertainties in the size and shape of the electrodes.

### TABLE II: Parameters of the generalized Drude-Lorentz model

| $\omega_0$ | $\omega_p$ | $\gamma$ | $\theta$ | $\Delta\varepsilon$ | $\omega_{0}^{\text{calc}}$ |
|-----------|-----------|---------|--------|-------------|-----------------|
| 147/168 | 348/342 | 1.1/ 5.4 | 3.99/4.12 | $T^\prime$ | 156 |
| 309/306 | 133/110 | 2.3/4.2 | 0.18/0.13 | $\tau + \delta_{ac}$ | 246 |
| 341/341 | 501/494 | 1.5/4.2 | $2.15/2.11$ | $\delta_{ac} + \tau$ | 410 |
| 419/416 | 308/288 | 5.2/11.5 | 0.54/0.48 | $\delta_{as} + \tau$ | 455 |
| 500/498 | 513/518 | 9.2/21.0 | 1.05/1.08 | $\nu_{as} + \delta_{sc}$ | 547 |
| 664/663 | 756/759 | 11.5/21.8 | 1.30/1.31 | $\nu_{as}$ | 671 |
| 859/860 | 425/422 | 6.2/10.0 | 0.24/0.24 | $\nu_{as}$ | 837 |

The mode with $\theta_1 = 72^\circ$ gives rise to the peculiarily feature peak at about 375 cm$^{-1}$ for $\chi = 0^\circ$ and $30^\circ$. The sixth mode at $\omega_{0,6} = 455$ cm$^{-1}$ is well separated in frequency from all other modes and thus can be observed easily for all values of $\chi$ considered here. Due to the strong orientational dispersion of $\varepsilon_{ac}(\omega)$ in the vicinity of this mode (see below), it also affects $R_{ac}(\omega, 90^\circ)$ although $\omega = 90^\circ$ is almost orthogonal to its orientation $\theta_0 \approx 0^\circ$.

The case of $E \perp b$ requires a more careful analysis. The interplay of partially overlapping modes with different rotation angles $\theta_i$ gives rise to complex line shapes in $R_{ac}(\omega, \chi)$ (see Figs. 3 and 4). Therefore it is more difficult to disentangle the contributions of the different modes. We find that the data can be described by a sum of eight $B_u$ modes, as predicted by the factor-group analysis for $T > 12.5$ K (see Eq. [2]). Eight separate $B_u$ modes are most easily recognizable in the data of $R_{ac}(\omega)$. However, the eigfrequencies can be read off more easily from $R_{ac}(\omega, \chi)$. Five of the eigfrequencies have an eigfrequency lower than 300 cm$^{-1}$, see Tab. [1]. Four out of these five modes can be easily recognized in the spectrum of $R_{ac}(\omega)$ for $\chi = 0^\circ$ below 300 cm$^{-1}$ at $T = 10$ K (see Fig. 7). These four modes have the eigfrequencies $\omega_{0,1} = 139$ cm$^{-1}$, $\omega_{0,2} = 201$ cm$^{-1}$, $\omega_{0,3} = 241$ cm$^{-1}$, and $\omega_{0,5} = 283$ cm$^{-1}$. The mode with $\omega_{0,4} = 273$ cm$^{-1}$ has a much larger oscillator strength, giving rise to the pronounced Reststrahlen band observed between about 250 cm$^{-1}$ and 400 cm$^{-1}$ for $\chi = 90^\circ$. The eigfrequencies $\omega_{0,1} = 237$ cm$^{-1}$ have a much larger oscillator strength, giving rise to the pronounced Reststrahlen band observed between about 250 cm$^{-1}$ and 400 cm$^{-1}$ for $\chi = 90^\circ$. The eigfrequencies $\omega_{0,4} = 273$ cm$^{-1}$ correspond to the low-frequency edge of the Reststrahlen band, whereas the steep drop of $R_{ac}(\omega, 90^\circ)$ at about 390 cm$^{-1}$ can be identified with its longitudinal eigenfrequency (see Secs. IV and V C for a discussion of the mixing of LO and TO modes). This mode with $\theta_1 = 72^\circ$ gives rise to the peculiar feature peak at about 375 cm$^{-1}$ for $\chi = 0^\circ$ and $30^\circ$. The sixth mode at $\omega_{0,6} = 455$ cm$^{-1}$ is well separated in frequency from all other modes and thus can be observed easily for all values of $\chi$ considered here. Due to the strong orientational dispersion of $\varepsilon_{ac}(\omega)$ in the vicinity of this mode (see below), it also affects $R_{ac}(\omega, 90^\circ)$ although $\omega = 90^\circ$ is almost orthogonal to its orientation $\theta_0 \approx 0^\circ$.

Modes number seven and eight determine $R_{ac}(\omega)$ between 500 and 900 cm$^{-1}$. With $\theta_2 = 123^\circ$ and $\theta_3 = 34^\circ$, these two modes are nearly orthogonal to each other. Accordingly, $R_{ac}(\omega, 30^\circ)$ predominantly shows the higher mode with $\omega_{0,8} = 767$ cm$^{-1}$. The signature of the lower mode will be most pronounced for $\chi \approx \theta_7 = 123^\circ$, whereas the measured data sets with $\chi = 0^\circ$, 60$^\circ$, and 90$^\circ$ show complicated line shapes which reflect the existence of both modes. Note that the pronounced peak at about 750 cm$^{-1}$ for $\chi = 0^\circ$ does not require to invoke a further infrared-active mode. This peak is located right at the frequency of the steep drop of $R_{ac}(\omega, 90^\circ)$, i.e., at the longitudinal eigenfrequency of mode seven with $\omega_{0,7} = 554$ cm$^{-1}$ (see also Fig. 3). For comparison, it is instructive to consider again the nearly triangular hump around 375 cm$^{-1}$ for $\chi = 0^\circ$ which stems from the phonon mode with $\theta_1 = 72^\circ$. Similarly, the peculiar shape of the peak at 750 cm$^{-1}$ for $\chi = 0^\circ$ or 60$^\circ$ (see Figs. 3 and 4) originates from the phonon mode with $\theta_1 = 123^\circ$, i.e., roughly ±60° different from the value of $\chi$. Moreover, lattice dynamical calculations (1) for MnWO$_4$ predict only two $B_u$ modes above 500 cm$^{-1}$, namely at 576 cm$^{-1}$ and 777 cm$^{-1}$, in reasonable agreement with our experimen-
FIG. 5: (Color online) Reflectance of MnWO$_4$ at $T = 10$ K (black) and generalized Drude-Lorentz fit (red). a) - c) $R_{ac}(\omega, \chi)$ for different polarization angles $\chi$ as defined in Fig. 3, d) Reflectance $R_p(\omega, 11^\circ, 80^\circ)$ for $p$-polarized light incident within the (010) plane with $E \perp b$, see Fig. 2a) and Eq. 15, e) Reflectance $R_0(\omega)$ for $E \parallel b$.

FIG. 6: (Color online) Reflectance of MnWO$_4$ at $T = 295$ K (black) and generalized Drude-Lorentz fit (red). a) - c) $R_{ac}(\omega, \chi)$ for different polarization angles $\chi$, d) $R_p(\omega, 11^\circ, 80^\circ)$, e) $R_b(\omega)$.

The existence of eight $B_u$ modes is corroborated by the data for $R_p(\omega, \alpha, \varphi)$ measured with $p$-polarized light and (010) as plane of incidence [see panels (d) of Figs. 5 and 6 and Eq. 15]. In particular, $R_p$ shows the five lowest modes clearly separated from each other and only two $B_u$ modes above 500 cm$^{-1}$. For this measurement geometry, the modes show a strong LO-TO mixing, and the character changes from predominantly transverse to predominantly longitudinal as a function of the orientation angle $\theta$ of the mode with respect to the wave vector $k$. Accordingly, both the apparent peak position and the oscillator strength depend strongly on the angle of incidence $\alpha$ and on the angle $\varphi$, which describes the orientation of the ac plane with respect to the surface [see Fig. 2a) and Eq. 15]. This explains in particular the pronounced changes between $R_{ac}(\omega)$ and $R_p(\omega)$ observed for modes 4 and 8: $R_p(\omega, 11^\circ, 80^\circ)$ shows the high-frequency edges of the phonon modes (i.e., the LO frequencies) at the same frequencies as $R_{ac}(\omega, \chi)$, but the apparent oscillator strength is very different in $R_p$ and $R_{ac}$. As a result, all eight $B_u$ modes are clearly separated from each other in $R_p$, but the apparent order of modes 4 and 5 is reversed. The weak mode 5 gives rise to a feature close to $\omega_{0.5} = 283$ cm$^{-1}$ also in $R_p$, but the much stronger mode 4 with $\omega_{0.4} = 273$ cm$^{-1}$ appears as a band between 300 and 400 cm$^{-1}$ in $R_p$. With small exceptions, our fit describes both $R_p(\omega, \alpha, \varphi)$ and $R_{ac}(\omega, \chi)$ very well. This clearly demonstrates that $\varepsilon_{ac}(\omega)$ has been determined correctly (cf. Sec. V C).
A Kramers-Kronig-constrained variational analysis of $R_{ac}(\omega, \chi)$ for $\chi \in \{0^\circ, 30^\circ, 90^\circ\}$ (see Sec. IV D) supports our results from the generalized Drude-Lorentz model for the number of modes and for the properties of the lower seven modes. Figure 8 compares $\text{Im}\{\varepsilon_{xx}(\omega)\} + \text{Im}\{\varepsilon_{zz}(\omega)\}$ obtained by the two approaches. Also the Kramers-Kronig-constrained variational analysis shows four strong $B_u$ modes below 300 cm$^{-1}$, a weak feature that corresponds to the mode at $\omega_{B_u,5} = 283$ cm$^{-1}$ (see insets of Figs. 8 and 9), one mode at about 450 cm$^{-1}$, and two modes above 500 cm$^{-1}$. The Kramers-Kronig-constrained variational analysis employs a fixed line width and thus encounters problems to precisely describe the phonon modes number 1 and 3 with line widths smaller than 1 cm$^{-1}$. This explains the spike observed at about 154 cm$^{-1}$ in Fig. 8.

The results of the two approaches for the diagonalized form of the real part of the dielectric function $\text{Re}\{\varepsilon_{ac}\}$ are given in Fig. 9 for the high-frequency range. The main discrepancy between the generalized Drude-Lorentz model and the Kramers-Kronig-constrained variational approach is observed for the line shape of the highest $B_u$ mode (see Sec. V C).

The rotation angles $\phi_{\text{Im}}(\omega)$, $\phi_{\text{Re}}(\omega)$, and the angles $\theta_i$ of the different oscillators of the generalized Drude-Lorentz model are plotted in Fig. 10. Below 500 cm$^{-1}$, MuWO$_4$ shows a pronounced orientational dispersion of $\varepsilon_{ac}(\omega)$. The two high-energy modes above 500 cm$^{-1}$ originate from stretching/bending vibrations of W-O bonds of the tightly bound WO$_6$ octahedra. Remarkably, the rotation angles $\theta_1 = 123^\circ$ and $\theta_8 = 34^\circ$ of these two modes agree nicely with the projections of the W-O bonds on the ac plane, see Fig. 1. The O(2)-O(2) edge of the WO$_6$ octahedra is rotated by about 30$^\circ$ with respect to the x axis, and the rotation of the shorter O(1)-W-O(1) bond (light red bonds in Fig. 1) amounts to about 123$^\circ$.

In total, we have identified both the seven $A_u$ modes and the eight $B_u$ modes predicted by a factor-group analysis. This has been claimed before both by Choi et al.\textsuperscript{[20]} and by Maczka et al.\textsuperscript{[21]} but both studies investigated only two polarization directions within the ac plane. Our analysis demonstrates that this is clearly not sufficient to determine the modes with $B_u$ symmetry in this monoclinic compound. In the analysis of the single-crystal data of Maczka et al.\textsuperscript{[21]} modes are missing at 273, 283,
FIG. 9: (Color online) The two entries of the diagonal form of the real part \( \Re \{ \hat{\varepsilon}_{ac}(\omega, \chi) \} \) at 10 K as obtained from a generalized Drude-Lorentz fit (gDL, black lines, cf. Eq. 6), a Kramers-Kronig-constrained variational analysis of \( R_{ac}(\omega, \chi) \) (KKvar, red lines, cf. Sec. IV D), and a fit using an asymmetric, non-Lorentzian line shape for the highest \( B_u \) mode (blue dashed lines, cf. Eq. 12). Insets: same data on an enlarged scale.

and 554 cm\(^{-1}\) in Mn\(_{0.85}\)Co\(_{0.15}\)WO\(_4\) and at 201, 273, and 455 cm\(^{-1}\) in Mn\(_{0.97}\)Fe\(_{0.03}\)WO\(_4\). Partially, these modes have been observed in the polycrystalline samples\(^{13}\) Choi et al.\(^{19}\) reported 8 frequencies for \( E \parallel a \) and 6 more frequencies for \( E \parallel c \). 5 (4) of them nearly degenerate with the ones reported for \( E \parallel a \) (b). Our data reveal that several of these modes are actually \( A_u \) modes, whereas the \( B_u \) modes at 273, 283, 554, and 767 cm\(^{-1}\) are missing. At first sight, it may seem surprising that in particular the modes with large oscillator strength at 273 cm\(^{-1}\) and at 554 cm\(^{-1}\) have been overlooked. However, our reflectivity data show that in particular the line shapes of the strong modes with large LO-TO splitting – giving rise to spectral overlap with other bands\(^{20}\) – depend strongly on the angle \( \chi \). Moreover, the reflectivity spectrum of the \( B_u \) modes strongly depends on the measurement geometry, i.e., on the direction of the wavevector. Weaker modes give rise to sharper features, which facilitates the determination of their eigenfrequencies.

C. Line shape of the highest \( B_u \) mode

The line shape of \( R_{ac}(\omega, \chi) \) is not described very well between about 700 and 800 cm\(^{-1}\) if we stick to eight modes with a Lorentzian line shape (see Fig. 11). We emphasize that adding a further Lorentzian mode to \( \hat{\varepsilon}_{ac}^{\text{DL}}(\omega) \) in Eq. 6 does not significantly improve the quality of the fit. The steep drop of the Reststrahlen band at about 900 cm\(^{-1}\) indicates a small value of the damping \( \gamma_8 \) of the eighth \( B_u \) mode, whereas the much more gradual rise at the low-frequency side of this mode between 700 and 800 cm\(^{-1}\) for \( \chi = 30^\circ \approx \theta_8 \) is a clear signature of a larger damping. Accordingly, a fit based on Eq. 12 with an asymmetric line shape for the mode with \( \omega_0,8 = 767 \text{ cm}^{-1} \) yields a much better description of \( R_{ac}(\omega, \chi) \) (cf. blue lines in Fig. 11). The fit parameters are given in Table III. An asymmetric line shape is supported by the Kramers-Kronig-consistent variational analysis of \( R_{ac}(\omega, \chi) \) (see Figs. 8 and 9).

In contrast to \( R_{ac}(\omega, \chi) \), \( R_p(\omega) \) is described very well by the generalized Drude-Lorentz model (red line in panel d) of Fig. 11. In fact, the description of the highest \( B_u \) mode in \( R_p(\omega) \) becomes slightly worse if we use the asymmetric oscillator model, which overestimates the absolute value of \( R_p(\omega) \) at the maximum of the highest mode at about 880 cm\(^{-1}\). This is a compromise of the fit which aims at a simultaneous description of \( R_{ac}(\omega, \chi) \) and \( R_p(\omega) \). Note that the agreement between \( R_{ac}(\omega, \chi) \) and the fit is not improved significantly if we fit only
Δε(ω,χ) with χ ∈ {0°, 30°, 90°} were fitted simultaneously. Black: measured reflectance data. Inset: highest $B_u$ mode on an enlarged scale.

$R_{ac}(ω, χ)$ but not $R_p(ω)$.

One possible source for the asymmetric line shape in $R_{ac}(ω, χ)$ is a mixing of transverse and longitudinal modes. Our analysis of $R_{ac}(ω, χ)$ assumes that only transverse modes are excited, which is valid for normal incidence. This assumption thus may break down for an angle of incidence of α = 11°. In the analysis of $R_p(ω, α, ϕ)$, the finite value of ρ and the mixing of longitudinal and transverse modes are taken into account, see Eq. [15]. The mixing of transverse and longitudinal character is particularly strong if the corresponding eigenfrequencies are nearly degenerate. The near degeneracy of $ω_{LO,7}$ and $ω_{0,8}$ is apparent from Fig. 9 which shows the two entries of the diagonal form of the real part Re{ξ_{ac}(ω)}. The two zero crossings of the diagonal components which correspond to $ω_{LO,7}$ and $ω_{0,8}$ nearly coincide in frequency at roughly 760 – 770 cm$^{-1}$. This is the frequency range with the largest deviations between $R_{ac}(ω, χ)$ and the Lorentzian fit. In this range, Re{ξ_{ac}(ω)} is close to zero in any direction within the $ac$ plane. We propose that this causes the unusual line shape.

In $R_p(ω, α, ϕ)$ with ϕ = 80°, the highest $B_u$ mode predominantly shows longitudinal character, giving rise to only a small peak close to $ω_{LO,8}$. The eigenfrequency of this predominantly longitudinal mode does not coincide with $ω_{LO,7}$, thus the mixing of $B_u$ modes 7 and 8 does not play a role for this geometry. Accordingly, $R_p(ω, 11°, 80°)$ is well described by a model employing a constant value of $γ_8$.

**D. Temperature dependence**

1. $A_u$ modes

The Drude-Lorentz fit parameters of all $A_u$ phonon modes are plotted as a function of temperature in Fig. 12. Above 20 K, all parameters evolve smoothly with temperature, there is no evidence for any strong anomaly. Six of the seven $A_u$ modes soften by only 1% or less between 10 K and 295 K. The lowest $A_u$ mode with $ω_{0,1} = 174$ cm$^{-1}$ forms an exception. Between 10 K and 295 K, it softens by 5.6 cm$^{-1}$ or 3%, showing the largest redshift for $E \parallel b$ both on a relative and an absolute scale. This pronounced shift can be seen clearly in the reflectivity data, see Fig. 7. In Raman data, the largest relative shift of 2.5% between 5 K and 300 K is observed for the lowest $A_u$ mode. In case of the $B_u$ modes, the largest relative redshift is observed for the two lowest modes (see below). The phonon softening observed above 20 K can be attributed to the typical thermal expansion of the lattice, reflecting anharmonicity. The damping constants $γ_i$ of all $A_u$ modes behave...
phonon parameters of the $A_u$ modes. We focus on the mode with $\omega_{0,1}(10\,\text{K}) = 174\,\text{cm}^{-1}$, which shows the largest changes of $\epsilon_{0,i}, \omega_{p,i}$, and $\Delta \epsilon_i$ at low temperatures. Figure 13 shows the temperature dependence of $\omega_{0,1}$ and of $\omega_{p,1}$ on an enlarged scale. The changes of $\omega_{0,1}$ between the different phases amount to only $0.1–0.2\,\text{cm}^{-1}$ or $0.1\%$, which is hard to resolve experimentally. However, the values for $\omega_{0,1}$ found at $10\,\text{K}$ and $13\,\text{K}$ clearly deviate from the approximately quadratic temperature dependence of $\omega_{0,1}$ observed above $20\,\text{K}$. In particular, the hardening of $\omega_{0,1}$ with decreasing temperature is the opposite of the conventional phonon mode softening occurring in proper ferroelectrics. At the same time, spin-phonon coupling is expected to cause a phonon shift proportional to the nearest-neighbor spin-spin correlation function $^{70-74}$ For the spectral weight we find a reduction of $\Delta \omega_{p,1}^2 = [\omega_{p,1}(13\,\text{K})]^2 - [\omega_{p,1}(10\,\text{K})]^2 \approx 6 \cdot 10^2\,\text{cm}^{-2}$, see Fig. 13. Note that this corresponds to only $0.5\%$ of $\omega_{p,1}^2$. Together, the decrease of $\omega_{p,1}^2$ and the increase of $\epsilon_{0,1}$ between $13\,\text{K}$ and $10\,\text{K}$ yield a reduction of the oscillator strength $\Delta \epsilon_1$ of about $0.03$ (see red dots in Fig. 14). Note that the sum of the changes of all other modes including the change of $\epsilon_{\infty}$ is about an order of magnitude smaller. According to the sum rule, the spectral weight $\Delta \omega_{p,1}^2$ is either transferred to the electromagnon at low frequencies or to high frequencies. If $\Delta \omega_{p,1}^2$ was fully transferred to the electromagnon, and if we use a magnon eigenfrequency of $\omega_{0,\text{em}} \approx 3 – 4\,\text{cm}^{-1}$ as observed in inelastic neutron scattering $^{75,76}$ then the electromagnon should show an oscillator strength of $\Delta \epsilon_{\text{em}} = \Delta \omega_{p,1}^2/\omega_{0,\text{em}}^2 \approx (4 - 7) \cdot 10^1$. In the following, we will use low-frequency data to demonstrate that the oscillator strength of the electromagnon is much smaller.

Figure 14 shows the temperature dependence of the real part Re($\epsilon_i$) measured by dielectric spectroscopy at $45\,\text{MHz}$ and $96.8\,\text{kHz}$. We have chosen these frequencies for two reasons. First they are far below the eigenfrequency of the electromagnon, at least for temperatures not too close to the phase transition at $T_{N2}$, see below. Second they are high enough to neglect contributions from domain-wall dynamics $^{77}$ Therefore, differences between Re($\epsilon_i$) at $45\,\text{MHz}$ and the value determined from the phonon parameters have to be attributed to the electromagnon contribution. At $T_{N1} \approx 6.5 – 8.0\,\text{K}$ the low-frequency data show a jump of Re($\epsilon_i$) of about $0.01$, in agreement with the results of Refs. $^{8}$ and $^{9}$. The peak in the vicinity of $T_{N2}$ reflects the washed out divergence of Re($\epsilon_i$) at the phase transition. This can be attributed to the critical slowing down of dielectric fluctuations $^{31}$ Since the phonons do not show any softening, it has to be the softening of the electromagnon – or, above $T_{N2}$, of the related fluctuations – which gives rise to an enhancement of $\Delta \epsilon_{\text{em}} = \omega_{p,\text{em}}^2/\omega_{0,\text{em}}^2$, in the immediate vicinity of the phase transition at $T_{N2}$. Between $13\,\text{K}$ and $10\,\text{K}$, the phonon oscillator strength decreases by about $\Delta \epsilon_1 = 0.03$, as discussed above, whereas Re($\epsilon_i$) changes by about $0.01$. The difference between these two values offers a rough estimate of the electromagnon os-

as expected, showing a smooth increase with increasing temperature. Again, the strongest change (on a relative scale) is observed for the lowest $A_u$ mode. The oscillator strength $\Delta \epsilon_i$, i.e., the contribution of a given mode $i$ to the real part of $\epsilon_b$ at sub-phonon frequencies, is obtained via $\Delta \epsilon_i = (\omega_{p,i}/\omega_{0,i})^2$. On a relative scale, the $A_u$ mode at $309\,\text{cm}^{-1}$ shows the most pronounced reduction of $\Delta \epsilon_i$ with increasing temperature, but this mode also has the smallest absolute value of $\Delta \epsilon_i$ (see Tab. IV and Fig. 7). According to Maczka et al. $^{31}$ this mode corresponds to a WO$_2$ bending mode (twisting and scissoring, see Tab. IV). Note that the observed phonon softening with increasing temperature leads to an enhanced oscillator strength $\Delta \epsilon_i$. A decrease of $\Delta \epsilon_i$ with increasing temperature reflects that the increase of $1/\omega_{0,i}^2$ is overcompensated by a reduction of the spectral weight $\propto \omega_{p,i}^2$, i.e., of the effective ionic charge.

Below $20\,\text{K}$, we observe only small changes of the
cillator strength of $\Delta \varepsilon_{em} = 0.02$ at 10 K. For $\omega_{0,em} \approx 3-4 \text{ cm}^{-1}$ \cite{7570}, this yields a tiny oscillator strength of $\omega_{p,em}^2 \approx 0.2-0.3 \text{ cm}^{-2}$. This is about 6 orders of magnitude smaller than the oscillator strength $\omega_{p,1}^2$ of the lowest $A_u$ phonon mode, and still more than 3 orders of magnitude smaller than the small reduction of $\omega_{p,1}^2$ observed between 13 K and 10 K. We thus may safely conclude that the spectral weight of the phonons is almost entirely transferred to higher frequencies at the phase transition.

We conclude that the spin-lattice interaction is not strong enough in MnWO$_4$ to change the phonon spectra substantially at the magnetic phase transitions. Nevertheless we are able to resolve small changes of the $A_u$ mode lowest in energy. Note that also in the manganites AMnO$_3$ (with $A = \text{Gd}_{1-x}\text{Tb}_x$ and Eu$_{1-x}\text{Y}_x$) it is the phonon mode lowest in energy which is most affected by the transition to the multiferroic phase\cite{25,21}. Contrary to the conventional phonon softening observed in proper ferroelectrics, the hardening of phonons at the transition to the multiferroic phase may turn out to be a characteristic property of multiferroics\cite{39,22}.

2. $B_u$ modes

Figure \ref{fig:15} shows the temperature dependence of the parameters of the generalized Drude-Lorentz fit for all $B_u$ phonon modes between 10 K and 295 K. The overall picture is very similar to the case of the $A_u$ modes. Six of the eight $B_u$ modes soften with increasing temperature, and the largest relative redshift between 10 K and 295 K is observed for the two modes lowest in energy. The two modes with $\omega_{B,4} = 273 \text{ cm}^{-1}$ and $\omega_{B,8} = 767 \text{ cm}^{-1}$ show an unexpected increase of the eigenfrequency with increasing temperature. For the highest $B_u$ mode with $\omega_{B,8} = 767 \text{ cm}^{-1}$, we attribute this behavior to the fact that the line shape of $R_{ac}(\omega)$ is not described very well by the generalized Drude-Lorentz model, as discussed above. The deviations between fit and measured data for $R_{ac}(\omega,30^\circ)$ at about $750 \text{ cm}^{-1}$ [panel b) in Figs. 5 and 6] show that $\omega_{B,8}$ cannot be determined with the same precision as the eigenfrequencies of the other modes with a Lorentzian line shape.

The damping constants $\gamma_i$ of all $B_u$ modes increase with increasing temperature. Similar to the $A_u$ modes, most $B_u$ modes show a modest increase of less than a factor 2, while the two modes lowest in energy show a more pronounced temperature dependence. The temperature dependence of the rotation angles $\theta_i$ is only moderate, for seven modes the value of $\theta_i$ is stable within 2°. A more detailed analysis of the rotation angles would require measurements for a larger number of polarization directions $\chi$. Finally, the temperature dependence of the oscillator strengths $\Delta \varepsilon_i$ is somewhat larger than observed for the $A_u$ modes. Remarkably, the mode with $\omega_{B,5} = 283 \text{ cm}^{-1}$ looses more than half of its oscillator strength between 10 K and 295 K (see also Fig. 7). Like in the case of the $A_u$ modes, this strong relative change of $\Delta \varepsilon_i$ is observed for the mode with the smallest value of $\Delta \varepsilon_i$.

Maczka et al. observed anomalies in the eigenfrequencies and damping constants of Mn$_{0.97}$Fe$_{0.03}$WO$_4$ and Mn$_{0.85}$Co$_{0.15}$WO$_4$ at about 50 K and around 150 to 200 K. These results were obtained from absorption measurements on polycrystalline samples, which were grown with a solvent, resulting in dark plates. The dark color of these samples may be caused by the dopants Fe and Co, but it may also indicate that not all Mn ions are in the divalent state, as it was found for flux-grown, undoped MnWO$_4$. In our ruby-red transparent MnWO$_4$ crystals, we do not find any evidence for anomalies above 20 K, neither for $B_u$ nor for $A_u$ phonon modes.

Below 20 K, we find only subtle changes close to the experimental uncertainty. For the $B_u$ modes, a precise determination of possible small changes of the oscillator

\[ E \perp b \]

\[ \omega_0(T) / \omega_0(10K) \]

\[ \theta(T) - \theta(10K) \ [\text{degree}] \]

\[ \Delta \varepsilon(T) / \Delta \varepsilon(10K) \]

\[ \gamma_i \]

\[ \chi \]

\[ \chi_{ac}(\omega,\chi) \]

\[ \Delta \varepsilon_i \]

\[ \gamma_i \]

\[ \theta_i \]

\[ \omega_{B,i} \]

\[ R_{ac}(\omega) \]

\[ \text{fit} \]

\[ \text{measured} \]

\[ \text{data} \]

\[ \text{fit} \]

\[ \text{measured} \]

\[ \text{data} \]

\[ \text{fit} \]

\[ \text{measured} \]

\[ \text{data} \]
strength $\Delta \varepsilon_i$ of oscillator $i$ is more difficult than for the $A_u$ modes because $\Delta \varepsilon_i$ is correlated to the value of the orientation $\theta_i$. The eigenfrequency $\omega_{0,1} = 139$ cm$^{-1}$ of the lowest $B_u$ mode hardens by about 0.05% between 20 K and 13 K and by about 0.13% across $T_N$ between 13 K and 10 K (see inset of Fig. 15). These values are very similar to the results obtained for the lowest $A_u$ mode.

VI. CONCLUSION

In monoclinic MnWO$_4$, we observed all infrared-active phonon modes and determined their temperature dependence. In agreement with a factor-group analysis, we found 7 $A_u$ modes and 8 $B_u$ modes. The phonons show only subtle changes at the magnetic phase transition between the AF2, AF3, and the paramagnetic phase. In particular, the eigenfrequency of the lowest $A_u$ mode increases by roughly 0.1% upon cooling from 13 K to 10 K, while the spectral weight decreases by $(\Delta \omega_{p,1}/\omega_{p,1})^2 \approx 0.5\%$. Comparison with data for the quasi-static dielectric constant $\text{Re} \{\varepsilon_b\}$ yields an upper boundary for the spectral weight of the electromagnon of less than 0.1% of the small change $\Delta \omega_{p,1}^2$ of the spectral weight of the lowest $A_u$ mode. A phonon hardening upon entering the multiferroic phase may turn out to be a characteristic property of magnetoelectric multiferroics of spin-spiral type. In contrast to previous reports on MnWO$_4$ or slightly doped Mn$_{1-x}$A$_x$WO$_4$, we do not find any anomalies above 20 K. We conclude that spin-lattice coupling in MnWO$_4$ is only small. The quantitative understanding of the phonon modes obtained here provides an excellent starting point for the analysis of the optical data of nanocrystals.$^{39,45}$

In general, a quantitative analysis of the reflectance of a monoclinic compound such as MnWO$_4$ is not an easy task. A careful analysis of the data is in particular important in case of overlapping modes. A full polarization analysis is an essential prerequisite for the identification of the correct number of modes and of their parameters. For phonon modes with $B_u$ symmetry, the combined analysis of $R_p(\omega)$ – measured with the (010) plane as plane of incidence – and $R_{ac}(\omega, \chi)$ is best suited for a reliable determination of $\hat{\varepsilon}_{ac}$ and of the phonon parameters. In the data on $R_{ac}(\omega, \chi)$ of MnWO$_4$, we found deviations of the expected Lorentz line shape around 750 cm$^{-1}$ in a frequency range where both Re$\{\varepsilon_{xx}\}$ and Re$\{\varepsilon_{zz}\}$ are close to zero. We derived a Kramers-Kronig-consistent oscillator model which is able to describe asymmetric line shapes in compounds with monoclinic symmetry. In particular, our model is also able to describe modes showing a gradual rise of $\text{Im} \{\varepsilon(\omega)\}$ at the low-frequency side and a steep drop at high energies. We propose that the asymmetric line shape observed in $R_{ac}(\omega, \chi)$ for near-normal incidence is caused by the mixing of longitudinal and transverse modes in a frequency range where Re$\{\varepsilon_{ac}\}$ $\approx 0$ for all directions within the ac plane.

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