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Infrared-active phonons in the ferrimagnetic and multiferroic phases of $FeCr_2S_4$: Evidence for structural distortions

J. Deisenhofer,[1] F. Mayr,[1] M. Schmidt,[1] A. Loidl,[1] and V. Tsurkan[1,2]

[1] *Experimentalphysik V, Center for Electronic Correlations and Magnetism, Institute for Physics, Augsburg University, D-86135 Augsburg, Germany*

[2] *Institute of Applied Physics, Academy of Sciences of Moldova, MD-2028 Chişinău, Republic of Moldova*

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We report on the temperature evolution of the infrared-active optical phonons in $FeCr_2S_4$ investigated by Fourier-transform infrared spectroscopy. The eigenfrequencies of the four triply degenerate infrared-active T_{1u} phonons of the room-temperature cubic spinel structure shift when entering into the ferrimagnetically ordered state below $T_C = 165$ K indicating strong spin-phonon coupling as reported earlier. A new mode at 200 cm^{-1} emerges below a temperature $T^* \simeq 115$ K and a splitting of the lowest-lying cubic phonon mode at about 120 cm^{-1} appears below the temperature $T_M \approx 60$ K associated with the onset of an incommensurate modulation of the magnetic structure. At the transition to the orbitally ordered and ferroelectric ground state at $T_{OO} = 9$ K two more modes emerge at 146 and 253 cm^{-1} in very good agreement with the eigenfrequencies of two of the cubic Raman-active phonon modes reported by Choi *et al.* [J. Phys. Condens. Matter **19**, 145260 (2007)]. These new modes are interpreted as signatures of a symmetry lowering with a loss of inversion symmetry to induce the multiferroic orbitally ordered ground state.

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I. INTRODUCTION

The compound $FeCr_2S_4$ is known to exhibit a cubic spinel structure at room temperature, where the Fe^{2+} ions ($3d^6$, $S = 2$) are in a tetrahedral S^{2-} environment and the Cr^{3+} ions ($3d^3$, $S = 3/2$) are on octahedral sites. A ferrimagnetic ordering of the Fe^{2+} and Cr^{3+} sublattices occurs below $T_C = 170$ K [1,2]. At $T_M = 60$ K and $T_{OO} = 9$ K further anomalies have been reported and associated with changes in the magnetic structure [2–8] and an orbital ordering transition [2,9–16], respectively. More recently, the existence of a ferroelectric polarization and, hence, its multiferroic nature was reported in the ground state below T_{OO}, together with a strong magnetic-field dependence of the polarization and dielectric properties [17,18]. These observations suggest a symmetry reduction and structural distortions in the ground state, but direct evidence for clear deviations from cubic symmetry remained evasive even in synchrotron x-ray [2] and neutron diffraction [17] experiments. Optical experiments are very sensitive to symmetry changes, because selection rules will be broken and new modes can become optically active. The IR active phonon modes of $FeCr_2S_4$ have been investigated previously [19–21], but no anomalies at $T_{OO} = 9$ K had been reported. In the case of the study on single crystals [21] coauthored by some of us, the use of Cl as a transport agent for crystal growth suppresses the orbital ordering transition [16]. As the splitting of modes and the new modes we report here are weak, we believe that the underlying lattice distortions in the single crystals studied previously were also strongly reduced and the new modes not observable in the reflectivity study. Therefore, in the present study we investigated polycrystalline samples obtained by a spark-plasma sintering method with a clear anomaly at $T_{OO} = 9$ K in the specific heat as shown in a previous publication [2].

II. EXPERIMENTAL DETAILS

For the optical study we used polycrystalline samples with a high density obtained by a spark-plasma sintering (SPS) technique as described in Ref. [2]. The density of the SPS sample was determined as 3.85 g/cm^3 by a pycnometric method, which is in very good agreement with the density of single crystals.

The ferrimagnetic transition occurs at $T_C = 165$ K and the orbital ordering transition at 9 K. The FIR reflectivity was determined in the frequency range 50–700 cm^{-1} using a Bruker Fourier-transform infrared spectrometer IFS 113, which was equipped with a He-flow cryostat ($5 \leqslant T \leqslant 300$ K).

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1(a) we show reflectivity spectra in the far-infrared regime for several selected temperatures. At room temperature the four infrared-active phonons $T_{1u}(j)$ ($j = 1, 2, 3, 4$) of the cubic spinel lattice are clearly visible and the spectra are in good agreement with previous studies [21]. When approaching the ferrimagnetic transition temperature upon cooling the four modes clearly shift as a result of usual lattice hardening and spin-phonon interaction in the vicinity of T_C, which has already been published beforehand [21]. Here we want to focus on the changes of the phonon spectra and the appearance of additional modes below T_C. In particular, changes occur for the lowest-lying $T_{1u}(1)$ mode which broadens and splits on passing through the temperature $T_M = 60$ K associated with the appearance of an incommensurate helical magnetic structure. The additional features are indicated by three blue arrows for the curve at 50 K and suggest a lifting of the threefold cubic degeneracy of the mode. In addition, at the lowest temperature in the orbitally ordered phase the black arrows

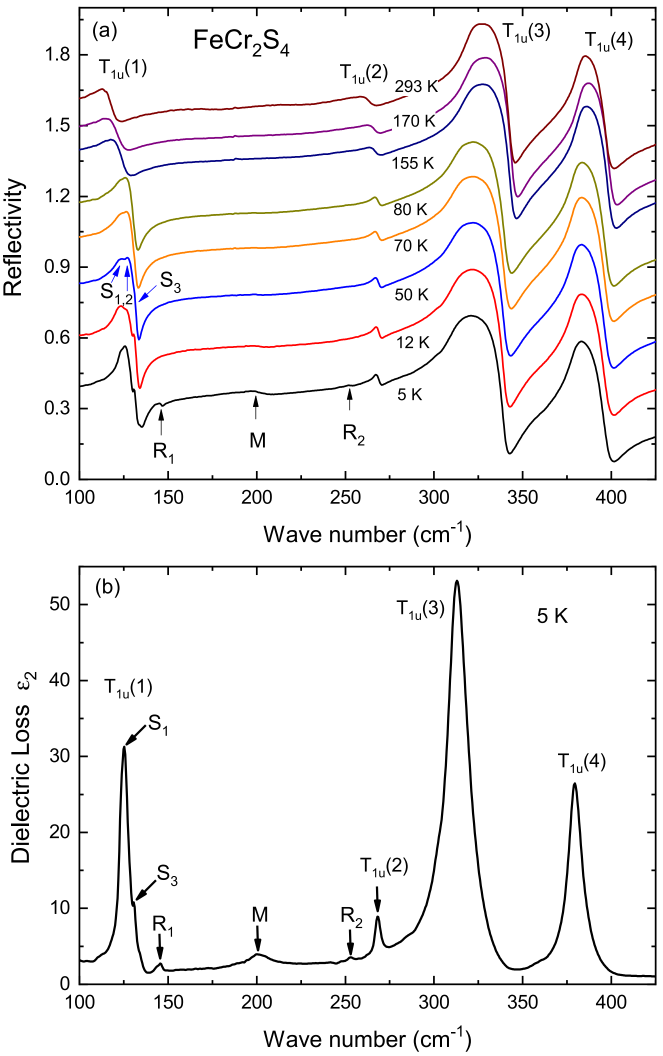

FIG. 1. (a) Reflectivity spectra of $FeCr_2S_4$ for selected temperatures above and below the transition temperatures. Arrows mark the appearance of a splitting of the lowest cubic phonon into three modes $S_{1,2,3}$ and the new modes M and $R_{1,2}$. The spectra are shifted by a positive offset with respect to the curve at 5 K. (b) Dielectric loss spectrum at 5 K as an example for the determination of the eigenfrequencies by the peak maxima.

indicate three more newly emerging features named R_1, M, and R_2. To track the detailed temperature dependence of the splitting and the appearance of the new modes, we determine the eigenfrequencies through the maxima of the dielectric loss spectra shown for the spectrum at 5 K in Fig. 1(b). The dielectric loss for all temperatures was obtained by using a Kramers-Kronig consistent variable dielectric function fitting routine [22] for our reflectivity spectra. Discernible changes take place in the frequency range from 100–260 cm^{-1}, which is highlighted in Fig. 2. The upper panel shows the dielectric loss for comparison at 12 and 5 K and assigns the maxima and the shoulder in the range of the cubic $T_{1u}(1)$ mode as split modes S_1, S_2, S_3, which is already visible below 50 K.

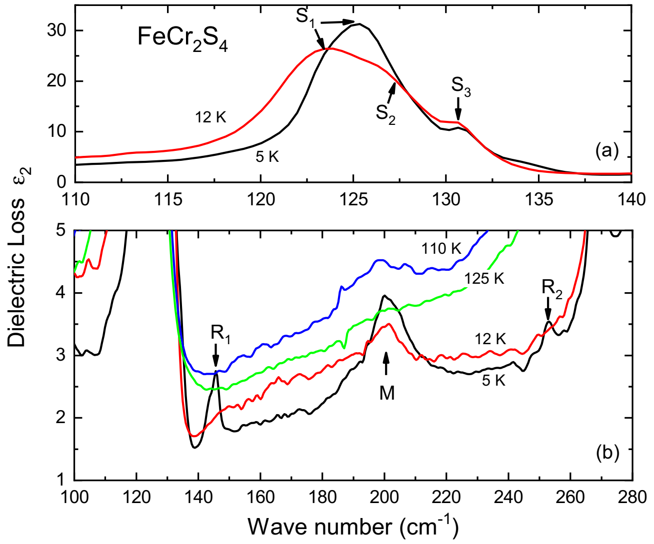

FIG. 2. Enlarged views of (a) the dielectric loss spectra of of lowest cubic $T_{1u}(1)$ phonon in $FeCr_2S_4$ for 5 and 12 K to reveal changes at $T_{\mathrm{OO}} = 9$ K and (b) the new modes M and $R_{1,2}$ appearing below T^* and T_{OO}, respectively. Arrows mark the determined positions of the split modes and the new modes.

In the orbitally ordered state at 5 K only two modes were assigned, because the lower-energy maximum does not exhibit a clear shoulder to distinguish between S_1 and S_2. The lower panel compares the same curves in the range of the modes R_1, M, and R_2 and clearly shows that R_1 and R_2 are only present in the orbitally ordered ground state below T_{OO}, while mode M is already present at 12 K and can actually be tracked as a very broad feature up to temperatures of about 110 K. An overview of all determined mode eigenfrequencies as a function of temperature is given in Fig. 3, indicating also the new energy scale related to the appearance of mode M at $T^* \simeq 115$ K.

In order to discuss the origin of these new modes, we compare all irreducible representations of the normal lattice modes in the cubic spinel structure with $Fd\bar{3}m$ given by

$$\begin{aligned} \Gamma &= 4T_{1u} && \text{(IR active)} \\ &\quad + A_{1g} + E_g + 3T_{2g} && \text{(Raman active)} \\ &\quad + 2A_{2u} + 2E_u + T_{1g} + 2T_{2u} && \text{(silent)} \end{aligned}$$

with theoretically derived values using lattice-dynamical calculations by Gupta *et al.* in Table I [23]. We use the eigenfrequencies of the IR active modes of this study and the ones of the Raman-active modes determined by Choi *et al.* [24], as both parameter sets are available at room temperature and at 5 K. The theoretical calculations [23] had been performed to reproduce the RT values and the agreement is reasonable. No new Raman modes had been detected with decreasing temperature, but we added to the Raman eigenfrequencies at 5 K the values of the new IR active modes R_1 and R_2, because of their coinciding eigenfrequencies with cubic T_{2g} and E_g modes. We believe that this is not accidental, but clear evidence for the loss of inversion symmetry in the system in the orbitally ordered ground state in $FeCr_2S_4$ and a prerequisite for the occurrence of a multiferroic ground state in $FeCr_2S_4$ [17,18]. The loss of inversion symmetry implies that phonon modes can become both Raman and IR active.

We would like to emphasize again that the deviation from the cubic symmetry is very small and could so far not

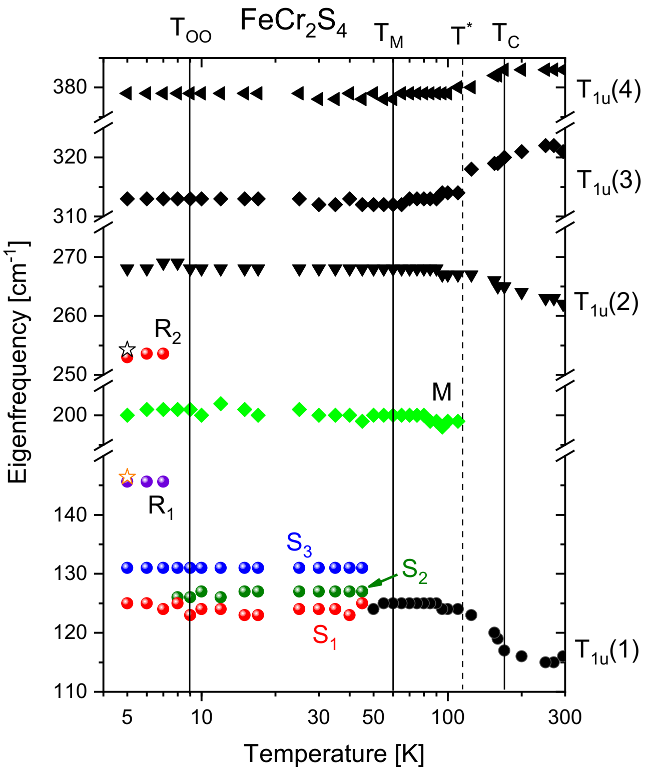

FIG. 3. Temperature dependence of the eigenfrequencies of the IR active modes (closed symbols) together with the eigenfrequencies of two Raman-active modes of the cubic structure at 5 K (open stars) taken from Ref. [24].

TABLE I. Experimental eigenfrequencies of IR-active phonons (this work) and Raman modes from Ref. [24] at room temperature and lattice dynamical calculations of the cubic modes from Ref. [23] in comparison to the IR active modes observed at 5 K in the orbitally ordered multiferroic ground state. The eigenfrequencies of the new IR modes M, R_1, R_2 at 5 K are compared to the cubic $E_u(1)$, $T_{2g}(1)$, E_g modes.

Irred. Rep.	IR (this work) and Raman [24] at 295 K	Calc. [23]	IR (this work) and Raman [24] at 5 K
$T_{1u}(1)$	116	117	125 (S_1), 131 (S_3)
$T_{1u}(2)$	262	220	268
$T_{1u}(3)$	321	339	313
$T_{1u}(4)$	383	388	379
A_{1g}	375.6	377	377.7
E_g	253	251	254.3 [24], 253 (R_2)
$T_{2g}(1)$	144.5	128	146.4 [24], 145.6 (R_1)
$T_{2g}(2)$	286	306	286.6
$T_{2g}(3)$	359	352	
$A_{2u}(1)$		263	
$A_{2u}(2)$		409	
$E_u(1)$		200	200 (M)
$E_u(2)$		365	
$T_{1g}(1)$		251	
$T_{2u}(1)$		138	
$T_{2u}(2)$		344	

be detected in any structural investigation. Therefore, it is straightforward to assume that also the normal modes of a distorted low-temperature structure will not differ too strongly from the cubic expectations. Having this in mind, we considered the theoretically derived values for the IR and Raman silent normal modes and found that a silent E_u-type mode is predicted to have an eigenfrequency of 200 cm^{-1}, coinciding with the IR active mode M appearing at $T^* \simeq 115$ K.

This almost perfect match of the eigenfrequencies may be somewhat accidental, as many of the other cubic modes show larger discrepancies between theory and experiment. However, given the electronic $3d^6$ structure of the Fe^{2+}, there is one hole residing in the degenerate e orbital, which couples to lattice vibrations of E_u or E_g type symmetry and shows Jahn-Teller type vibronic couplings as outlined in detail by Feiner *et al.* [12,25]. Notably, in the temperature regime below 125 K no evidence for a structural change has been reported. However, in several studies it had been noticed that changes occur below 120 K.

The magnetocrystalline anisotropy seems to change below this temperature as evidenced by susceptibility [5], electron spin resonance [3], and magnetization and time-resolved magneto-optical Kerr spectroscopy studies [26]. Moreover, the evaluation of the Fe-Mössbauer spectra by Kalvius *et al.* revealed the existence of a finite electric field gradient (EFG) in the magnetically ordered phase, which starts to increase monotonously when decreasing the temperature below 120 K [27]. The latter authors speculate about a minor lattice distortion occurring at this temperature, which does not alter the collinear spin arrangement but influences the electric quadrupolar field at the Fe nuclei. Such a scenario is consistent with our interpretation of mode M being of a symmetry which directly couples to the electronic e orbitals of the Fe ions. Hence, we assume that the appearance of mode M is a signature related to a subtle structural change, which might act as precursor for the transition to a noncollinear magnetic state below T_M.

The new modes at 146 and 253 cm^{-1} appear with the onset of the orbital ordering transition at $T_{OO} = 9$ K and are assigned to the cubic Raman-active modes of E_g and $T_{2g}(1)$ symmetry [23,28], respectively, which were observed at the same eigenfrequencies at 5 K [24].

Therefore, our optical study provides direct evidence for a sequence of symmetry reductions within the magnetically ordered regime. At $T^* \simeq 115$ K a cubic silent E_u mode becomes IR active as mode M and below T_S the lowest-lying cubic $T_{1u}(1)$ triplet splits into the three modes $S_{1,2,3}$. Finally, below the orbital ordering temperature, a loss of inversion symmetry is evidenced by the modes R_1 and R_2 at 146 and 253 cm^{-1}, which are both Raman and IR active, which is an important ingredient to understand the occurrence of the multiferroic ground state in $FeCr_2S_4$. The identification of the reduced symmetry group of the ground state is, however, not feasible from these observations in a polycrystalline sample.

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