# Paraelectromagnon in Multiferroic $CaMn_7O_{12}$ and Hybrid Ferroelectric Phase Transition in Multiferroic $Ca_3Mn_2O_7$

S. Kamba,[1] F. Kadlec,[1] V. Goian,[1] C. Kadlec,[1] C. Adamo,[2] H. Zhang,[3] K. Smith,[3] R. Beanland,[3] A.S. Gupta,[4] V. Gopalan,[4] J. Drahokoupil,[1] P. Vaněk,[1] M. Svatuška,[1] H. Seiner,[5] L. Palatinus,[1] M. Klementová,[1] N.A. Benedek,[6] I. Reaney,[7] K. Maca,[8] C.J. Fennie[2] and D.G. Schlom[2,9]

[1] Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic
[2] Cornell University, Ithaca, New York, USA
[3]University of Warwick, Gibbet Hill Road, Coventry, UK
[4]Pennsylvania State University, University Park, Pennsylvania, USA
[5] Institute of Thermomechanics, Czech Academy of Sciences, Prague, Czech Republic
[6]Materials Science and Eng. Program, The University of Texas at Austin Texas, USA
[7]University of Sheffield, Sheffield, UK
[8]Brno University of Technology, Brno, Czech Republic
[9] Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York, USA
*e-mail: kamba@fzu.cz*

Electromagnons are collective spin excitations occurring in magnetic phases of many magnetoelectric multiferroics. They contribute not only to the magnetic susceptibility but, due to dynamic magnetoelectric coupling, also to the off-diagonal components of the magnetoelectric susceptibility tensor. For that reason electromagnons are frequently considered as electrically active magnons. In the first part of this contribution we will show that electromagnons can persist in a paramagnetic phase, if there are short-range magnetic correlations. In analogy with paramagnons we propose to call such spin excitations *paraelectromagnons*.

We investigated spin and lattice dynamics of $CaMn_7O_{12}$ ceramics using infrared (IR), THz and inelastic neutron scattering (INS) spectroscopies in the temperature range 2 to 590 K, and, at low temperatures, in applied magnetic fields of up to 12 T.[1] Ferroelectric polarization in $CaMn_7O_{12}$, which appears at the antiferromagnetic phase transition, is the highest among all spin-induced ferroelectrics.[2] In the two antiferromagnetic phases below $T_{N1}$=90 K and $T_{N2}$ = 48 K, several IR-active excitations emerge below 90 cm$^{-1}$. Their frequencies correspond to the maxima in the magnon density of states obtained by INS. At the magnetic phase transitions, these modes display strong anomalies and, for some of them, a transfer of dielectric strength from the higher-frequency phonons is observed. We propose that these modes are electromagnons. Remarkably, at least one of these modes lying near 50 cm$^{-1}$ remains IR active in the paramagnetic phase; for this reason, we call it a paraelectromagnon. This mode becomes overdamped above 150 K, but it remains in the spectra at least up to 300 K. In accordance with this observation, quasielastic neutron scattering revealed short-range magnetic correlations persisting within temperatures up to 500 K above $T_{N1}$.

The second part of our contribution concerns our theoretical and experimental studies of $Ca_3Mn_2O_7$. Based on *ab initio* calculations, a new type of ferroelectric phase transition has been proposed in this material.[3] Supposedly, the ferroelectricity would be induced by freezing of two nonpolar phonons from the Brillouin zone boundary. If these modes of $X_2^+$ and $X_3^-$ symmetries freeze simultaneously, the *I4/mmm* phase transforms to an *A2₁am* orthorhombic structure; this phase transition would be called hybrid improper ferroelectric. If the modes freeze sequentially, the paraelectric *I4/mmm* phase should transform to an intermediate *Cmcm* or *Cmca* one (depending on if the $X_3^-$ or the $X_2^+$ mode freezes first); after freezing of the other order parameter, the ferroelectric *A2₁am* orthorhombic structure would finally appear. The same calculations have shown in $Ca_3Mn_2O_7$ films subjected to a biaxial compressive strain, switching of the polarization by the electric field should cause a 180°-flip of the magnetic moments by reversing the octahedral tilt.[3]

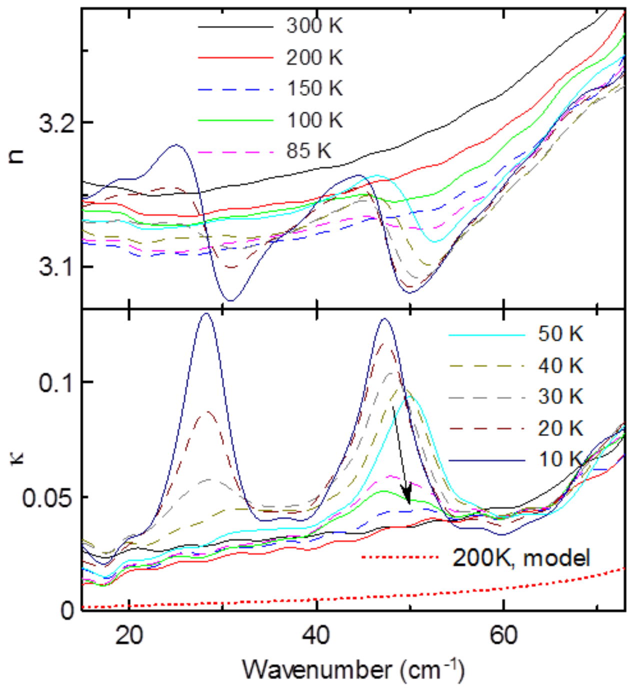


**Fig. 1.** Real and imaginary parts of the complex refractive index obtained by THz spectroscopy. The red dotted line in $\kappa(\omega)$ spectra shows the low-frequency wing from the phonons at frequencies above 90 $cm^{-1}$, obtained from fits. A heavily damped electromagnons (marked by arrow) is needed for the fit of experimental spectra above $T_{N1}$.

Thus, it is still an open question whether $Ca_3Mn_2O_7$ undergoes one hybrid or two successive phase transitions. Therefore we performed measurements using x-ray and electron diffraction, second harmonic generation (SHG), heat capacity, resonant ultrasound (RUS), and IR spectroscopy. We investigated bulk ceramics, unstrained and strained thin films. The thin films were deposited using MBE on (110) $YAlO_3$ and (110) $LuAlO_3$ single-crystal substrates.

The room-temperature electron and x-ray diffraction studies revealed the polar *A2₁am* crystal structure, but a rather high conductivity of the ceramics did not allow us to perform measurements of FE hysteresis loops nor a *T*-dependence of the radio-frequency permittivity. X-ray diffraction revealed an abrupt change in the lattice parameter near 670 K and the thermal expansion exhibited an anomaly around 630 K. Near 690 K, high-temperature selective-area electron diffraction and large-angle convergent-beam electron diffraction experiments found a single structural phase transition to the *I4/mcm* structure, but the polar clusters (probably with an *A2₁am* symmetry) persisted up to 900 K in approximately 1 volume percent of the sample. RUS experiment revealed two anomalies near 650 and 800 K. The first one can be explained by the structural phase transition and the second one by the disappearance of polar clusters (Burns temperature). Phonon anomalies seen in the IR spectra of ceramics and thin films supported a single structural change near 700 K. The square root of the SHG signal, which is proportional to the spontaneous polarization, linearly increased on cooling, which is typical for improper ferroelectrics. Thus, our data confirm the scenario of a hybrid ferroelectric phase transition in $Ca_3Mn_2O_7$.

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