Revealing strong magnon-photon coupling in a polar antiferromagnet Fe$_2$Mo$_3$O$_8$ by time domain terahertz spectroscopy

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Strong coupling between magnon and electromagnetic wave can lead to the formation of a coupled spin-photon quasiparticle named as magnon-polariton. The phenomenon is well studied for ferromagnetic systems inside microwave cavities in recent years. However, formation of magnon-polariton is rarely seen for an antiferromagnet (AFM) because the strong coupling condition is not easily fulfilled. Here we present time-domain terahertz measurement on a multiferroic polar antiferromagnet Fe$_2$Mo$_3$O$_8$. We find clearly beating phenomenon between two modes at frequencies slightly above and below the electric-active magnon frequency below $T_N$, which we assign to the formation of AFM magnon-polariton in the propagation of terahertz waves. However, the AFM magnon-polariton is absent in the frequency domain measurement. Our work reveals that the coherent magnon formation driven by the ultrashort THz pulse is a useful way for the realization of the strong coupling effect between photon and AFM magnon.

The strong coupling between light or electromagnetic wave and collective excitation of matter can produce a hybrid state or quasiparticle with energy levels different from either the electromagnetic wave or the collective excitation of matter. The hybrid state, being referred to as polariton, can be used to transfer information between the electromagnetic wave and collective excitation of matter, thus opening up new prospects for quantum control and information technology. Among different light-matter coupling quasiparticles, the magnon polariton, i.e., the hybrid light and magnon excitation in magnetically ordered material, has been anticipated and studied for a long time. However, due to the difficulty of achieving the strong coupling condition between spins of a magnet and electromagnetic wave, a clear hybridization effect could be hardly seen by traditional optical measurement. The magnon polariton was mainly inferred from the reflectance change within a very narrow frequency range in the reststrahl bands [1, 2]. The eminent strong coupling effect was realized only in recent years in ferromagnet (FM) systems (e.g. the traditional FM yttrium iron garnet) specifically inside a microwave cavity resonator where the magnon resonance frequencies were tuned via external magnetic field to approach the cavity resonance frequency [3–11]. Many applications have been proposed for spintronics and information processing technologies based on the realization of cavity magnon polariton.

Antiferromagnetic materials are expected to be more promising for future spintronics application, for an antiferromagnet (AFM) has much faster spin dynamics than a FM. The magnon in an AFM is in the terahertz frequency range due to the strong exchange interaction between the spin sublattices, whereas the magnon in a FM material is in the gigahertz frequency range. However, due to the absence of a net magnetic moment, the coupling of AFM to the electromagnetic fields of light is even weaker. Furthermore, the higher resonance frequency of AFM magnon makes both the stimuli and probe much more difficult by conventional electronics method. For those reasons, few work was reported on the magnon-photon coupling in AFM systems so far [12].

With the advance of ultrafast laser technique, time domain terahertz (THz) spectroscopy has emerged as a powerful tool to detect the dynamics of AFM magnons. The THz waves generated from femtosecond laser are phase stable electromagnetic pulses with time duration of ~ 1 ps. The THz electric field $E(t)$ can be detected by electric-optical (EO) sampling on a nonlinear crystal in the time domain. By Fourier transform of $E(t)$, the spectrum in frequency domain can be obtained. Time domain measurement has certain advantages. A particular advantage is that the dynamical responses from different excitations may be separated in different time windows or delays. The magnon signal can be smaller than the electronic signal, however, it usually has a long coherent time so that it can be separated from electronic signals. In this letter, we present time-domain terahertz measurement on a multiferroic polar AFM Fe$_2$Mo$_3$O$_8$. We find clearly beating phenomenon between two modes at frequencies slightly above and below the electric-active magnon frequency below $T_N$, which demonstrates the formation of AFM magnon-polariton in the propagation of terahertz electromagnetic wave. We further show that the AFM magnon-polariton is absent in the frequency domain measurement by using Fourier transform infrared spectrometer. We elaborate that the intrinsic high strength of electric active magnon and the coherent formation of magnon driven by the ultrashort THz pulses are key ingredients for the realization of the strong coupling effect between photon and AFM magnon.

Fe$_2$Mo$_3$O$_8$ is a well-known polar AFM magnet with the electric polarization along the c-axis. The single crystals of Fe$_2$Mo$_3$O$_8$ were grown by chemical vapor transport method similar to the previous reports[13, 14]. The resulted hexagonal crystals were characterized by X-ray diffractions, Laue patterns and magnetization measurement. The lattice and magnetic structure of Fe$_2$Mo$_3$O$_8$ in the AFM ordered phase are shown in Fig.1 (a). There are two types of Fe ions locating in octahedron and tetrahedron of O with different magnetic moments. The octahedrons and tetrahedrons share their corners to form a honeycomb lattice in the ab-plane. Figure 1
Due to the lack of inversion symmetry, there is no zero electric polarization present in the compound. A considerable electromagnetic effect was reported in the multiferroic state below $T_N$ [15, 16].

We performed time domain THz measurement on the crystals in a home built spectroscopy system with the terahertz beam normal to the ab-plane of the crystals. The terahertz radiation was generated from a large area GaAs photoconductive antenna by a mode locked Ti:sapphire femtosecond laser oscillator (center wavelength of 800 nm, pulse duration of 35 fs, and 80 MHz repetition rate) and detected by 1 mm ZnTe crystal via free space EO sampling method. Figure 2 (a) shows the waveforms of the transmitted THz electric field at several selected temperatures. Below $T_N$, we find long live oscillations after the main peak, which corresponds to the magnon mode at frequency 1.25 THz. This collective excitation mode has been studied in previous reports, however the time domain THz waveform within a sufficiently long time delay was not presented [17–19]. The polarization dependent measurements indicated this as an electromagnon of the antiferromagnetic spin system [17]. In general, the magnon excitation can be induced by an effective interaction through $dS_i/dt = [S_i, H_{eff}]$, where $H_{eff}$ reflects the interaction (e.g. Heisenberg interaction). Here, the magnetic excitation possesses in-plane (or perpendicular to the c axis) oscillation of electric polarization, which was proposed to be induced by the inverse Dzyaloshinskii-Moriya interaction and/or single-site anisotropy [17]. Because the mode is electric active, i.e. driven by the oscillating electric field rather than the magnetic field of the THz electromagnetic wave, the magnon strength is considerably higher than the usual magnon triggered by the magnetic dipole interaction.

In our experiment, a clear beating phenomenon from two modes close in energy was observed in the time domain spectrum below $T_N$ as presented in Fig. 2 (a). The signal intensity increases as the sample temperature decreases. As we shall explain that the beating is very likely to originate from the reversible energy exchange between THz wave and magnon mode, therefore is an indication of the Rabi oscillation from hybridized magnon-polariton state. We can get the spectrum in frequency domain through Fourier transformation of E(t) to study the interaction between the magnon mode and THz electromagnetic wave through the beating frequencies. There are two ways to get the spectrum in the frequency domain. One is to perform Fourier transformation of the E(t) in the whole time delays. In this way we get the spectrum of all the excitations, including the fast decayed excitations and the coherent collective excitations. The other one is to do the Fourier transformation of the time domain spectrum after the main peak. Then, the result is dominated by coherent collective modes. We perform Fourier transformation in both ways. The results for the lowest temperature at 4 K are shown in Fig. 2 (b) and (c), respectively. In the frequency domain spectrum transformed from all time delays, we can see only one dip at frequency of 1.25 THz, related to the absorption of the magnon excitation. In the frequency spectrum transformed from the dashed rectangular in Fig. 2 (a), which is the time window excluding the main peak, we can see two split peaks at 1.2 and 1.3 THz, respectively. Such beating phenomenon was rarely seen before. To the best of our knowledge, there was only one work reporting similar beating in TmFeO$_3$ [20]. There were two related studies on the hybridized coupling between magnon mode of Fe$^{3+}$ and the electron paramagnetic resonance of Er$^{3+}$ in ErFeO$_3$ [21] or simultaneously hybridized coupling of magnon-phonon-polariton in specially designed LiNbO$_3$-ErFeO$_3$ chip devices [22].

For a comparison, we also performed a frequency domain transmission spectroscopy measurement by using a Fourier transform infrared spectrometer (Bruker 80V) for the sample at the lowest temperature. The absorption spectrum is shown in Fig. 3. There exists only a single narrow absorption peak at 1.25 THz. Within the signal-to-noise ratio and spectral resolution, the peak does not show any splitting. The results exclude the intrinsic split of the magnon mode when a light passing through the sample, and show that the frequency domain measurement cannot afford the formation of the Rabi oscillation as observed in the time domain measurement.

We now discuss the underlying physics of observed beating

**FIG. 1.** (a) Crystal and magnetic structure of Fe$_2$Mo$_4$O$_8$. (b) The temperature dependent magnetization measurement for $H$/c-axis at 0.2 T.
phenomenon. As we mentioned in the introduction, the light matter interaction can lead to a hybrid state. According to Maxwell’s equation, the dispersion of electromagnetic wave can be obtained from the relation \[ k^2 - \omega^2 \varepsilon(\omega)\mu(\omega)] h_{em} = 0 \], where \( h_{em} \) represents the electromagnetic wave \[ 8 \]. The propagation of the wave in a media is dependent on the frequency \( \omega \), the permittivity \( \varepsilon \), and the permeability \( \mu \). In free space, the permittivity and permeability are constant. The \( k \) has a linear dispersion with \( \omega \). While in matters, the permittivity or permeability can be highly dependent on frequency due to the matter character. Especially, when the frequency of electromagnetic wave is resonant with the excitations such as a magnon, the electromagnetic wave can couple strongly to the excitation to form a hybridized state and open up a polariton energy gap.

The formation of the magnon polariton depends on the coupling strength. Because the coupling between electromagnetic wave and magnetic excitation through magnetic dipole interaction is usually weak, it is not easy to observe hybrid excitation by traditional optical techniques. In recent years, much progress has been made for realizing the magnon polariton in FM systems inside microwave cavities. The cavities were used to block the escape of microwave and to limit the energy of microwave around the magnetic matter. In such cavity magnon system, the magnon excitation absorbs the energy from the microwave inside the cavity. The excited magnon will decay by re-emitting photons \[ 23 \]. While the photons are limited in the cavity, they can be absorbed by the magnon again, and this leads to an energy circulation between magnon and microwave. In a real system, the energy may escape from the circulation. The imperfect mirrors will loss photons from the cavity, and the magnon may decay by other channels. If the energy exchange between magnon and microwave is more efficient than the escape of the microwave and the energy loss in the matter, the system is in strong coupling regime, resulting in cavity magnon polariton.

For an AFM, the magnon appears at much higher energy in THz frequency range. For this reason, the conventional cavity method based on the electronic technique in the microwave frequency regime is not applicable. Obviously, new techniques have to be developed to study the phenomenon. In the present time domain THz study, when the THz electromagnetic wave generated by the ultrafast laser pulse transmits through the sample, as illustrated in Fig. 4 (a), it transforms energy to the spin system and coherently excites the magnon, that is, the spins in different part of the sample undergo procession with the same phase. This is because the procession of each spin is triggered by the THz pulse and its phase is locked to the phase of THz pulse. The oscillations after the main peak in Fig. 2 (a) indicate the coherent magnon excitation in the time domain. With time delay, the excited coherent magnon decays by emitting THz electromagnetic wave. The emitted THz wave frequency is equal to the spin procession frequency, which can be absorbed again by the magnon. Once again the magnon emits THz wave. In this way the energy circle is built up, and a strong coupling condition is established. While the wave will eventually escape, but in picoseconds time scale we can clearly observe the decrease and increase of the THz amplitude, the beating phenomenon, reflecting the split modes with close frequencies. This is similar to a case of light interacting with a two-level system, resulting in a periodic change between absorption and stimulated emission of photons, which leads to Rabi oscillation. Such coupled spin-photon system can be described by the two-level Hamiltonian \[ 7, 9, 22 \].

\[
H = H_p + H_m + H_{int} = \hbar \left( \begin{array}{cc} qc & 0 \\ 0 & 0 \end{array} \right) + \hbar \left( \begin{array}{cc} 0 & 0 \\ \omega_0 - i\gamma & 0 \end{array} \right) + \hbar \left( \begin{array}{cc} 0 & \Omega/2 \\ \Omega/2 & 0 \end{array} \right).
\]

\( 1 \)

Here, \( H_p \) and \( H_m \) are the bare Hamiltonians of photon and magnon, \( H_{int} \) denotes their coupling, \( q \) the photon wavevector, \( c \) the speed of light in vacuum, \( \omega_0 \) the magnon frequency, \( \gamma \) the width of the magnon mode, \( \Omega \) the coupling strength. The eigenfrequencies are

\[
\omega_{\pm} = \frac{qc + \omega_0}{2} \pm i\frac{\gamma}{2} \pm \frac{1}{2} \sqrt{\Omega^2 + ((qc - \omega_0) + iy)^2}.
\]

\( 2 \)

As a result, the coupling leads to the splitting of two branches between the magnon and the THz wave, i.e. magnon-polariton. The splitting frequency at the resonant frequency...
\( \Omega \) is the Rabi frequency, reflecting the coupling strength. A plot of the dispersion of the coupled magnon-polariton from Eq. (2) with \( \omega_0=1.25 \) THz is shown in Fig. 4(b). The two dashed lines in Fig. 4(b) indicate the dispersion of photon and magnon without coupling. The light-matter coupling leads to the avoided crossing at resonant frequency, as shown by the red line. However, in frequency domain experiments, the continuous wave transmit through the sample, the detector records the averaged strength of the wave, can not afford the energy exchange process.

![THz waveform for two samples with thickness of 1 mm (sample 1) and 0.4 mm (sample 2) in time domain.](image)

**FIG. 5.** (a) THz waveform for two samples with thickness of 1 mm (sample 1) and 0.4 mm (sample 2) in time domain. (b) The Fourier transformed spectra in the frequency domain for the two samples. The beating period and signal strength vary with the thickness of the samples. The dash lines indicate the splitting of the modes for the 1mm thickness sample. A smaller splitting is seen for the thinner sample.

In fact, the coupling strength is enhanced for a assembly of N spins system. The coupling strength is known to be enhanced by a factor of \( \sqrt{N} \) \([4, 9, 21, 24]\). In the present study, the number of spins interacting with the THz electromagnetic wave transmitting through the sample should depend on the thickness \( l \) of the sample. Thus, we expect that the splitting of the modes \( \Omega \sim \sqrt{l} \). To testify the relation between the number of spins and the coupling strength, we performed the experiments on samples with different thickness. Figure 5 shows the THz spectra for two samples with thickness of 1 mm and 0.4 mm in both time and frequency domains at 4 K. Indeed, we observe a clear increase of beating period in the time domain and a reduction of the splitting in frequency domain for the thinner sample. The ratio of the splitting energy \( \Omega \) of the two samples is about 0.6, being consistent with the ratio of the square root of thickness \( \sim 0.63 \). The results confirm the positive correlation between spin number and coupling strength.

There are two points worth emphasizing before we conclude. First, in this multiferroic compound the AFM magnon is an electric active magnon. It couples to THz wave through electric dipole interaction rather than magnetic dipole interaction. The huge electric-magnetic coefficient of Fe\(_2\)Mo\(_3\)O\(_8\) makes the magnon to have rather strong signal strength. Second, the strong magnon signal level itself does not lead to a strong coupling to electromagnetic wave because the transmission measurement from FTIR does not lead to a level splitting. The phase-locking coherent excitation of large number of spins triggered by the ultrashort THz pulse is likely the origin for the formation of strong coupling effect.

To summarize, we studied the coupling effect between the THz electromagnetic wave and the electric active AFM magnon in Fe\(_2\)Mo\(_3\)O\(_8\). The level splitting or Rabi oscillation is invisible in frequency domain measurement but can be monitored by time domain THz spectroscopy experiment. A clear beating between two modes at frequencies slightly above and below the electric-active magnon frequency is observed below \( T_N \). We elaborate that the coherent formation of the spin procession enables the energy circulation in the propagation of the THz electromagnetic wave in the picoseconds time scale, thus establishing the strong coupling between the AFM magnon and THz light even without a cavity. The coupling strength is related to the assemple of spins, therefore, the thickness of samples. Our study further illustrates that the electric active magnon in multiferroics with strong electromagnetic effect is a proper candidate to study the strong coupling or magnon polariton, and the THz time domain technique is a promising tool for future study of information and energy transformation between photon and AFM magnon.

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