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The linear and nonlinear ac susceptibility measurements of Yb-pyrochlores, $Yb_2X_2O_7$ (X = Sn, Ti, and Ge), show transitions with a ferromagnetic nature at 0.13 and 0.25 K for $Yb_2Sn_2O_7$ and $Yb_2Ti_2O_7$, respectively, and an antiferromagnetic ordering at 0.62 K for $Yb_2Ge_2O_7$. These systematical results (i) provided information about the nature of the unconventional magnetic ground state in $Yb_2Ti_2O_7$; (ii) realized a distinct antiferromagnetic ordering state in $Yb_2Ge_2O_7$; and (iii) demonstrated that the application of chemical pressure through the series of Yb-pyrochlores can efficiently perturb the fragile quantum spin fluctuations of the Yb^{3+} ions and lead to very different magnetic ground states.

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The study of natural science has been increasingly focused on quantum phenomena. And the understanding of quantum phenomena is now at the forefront of modern condensed matter research. One celebrated example is quantum spin liquids (QSLs), in which a disordered, liquidlike spin state is led by quantum spin fluctuations. While the notion of QSL is now established in one-dimensional (1D) spin systems, realizing QSLs in dimensions greater than one has been a long-sought goal. Just recently, several materials with two-dimensional (2D) geometrically frustrated lattices, such as the triangular lattice and the kagome lattice, have been identified as QSLs (see references in [1]). It is urgent and of critical importance to understand the characteristic behavior of QSLs.

Therefore, as a potential three-dimensional (3D) QSL due to the effective $S = 1/2$ nature of the Yb^{3+} cations, the pyrochlore $Yb_2Ti_2O_7$ has recently received a lot of attention [2–7]. Several neutron scattering measurements [5,8,9] show no evidence of long-range magnetic ordering for $Yb_2Ti_2O_7$ but a magnetic ordered phase with an emergent spin wave excitation with applied magnetic fields above 0.5 T [10,11]. Related theoretical studies proposed it to be a Coulombic quantum spin liquid [11,12] or a model exchange quantum spin ice [13]. On the other hand, the specific-heat data [14] and the report of weak Bragg peaks [15,16] suggest that $Yb_2Ti_2O_7$ is ferromagnetically ordered around 0.24 K, which has been related to the Higgs mechanism [16]. Ross *et al.* pointed out that one possibility for these discrepancies could be the 1–2 % chemical disorder in single-crystal samples [17], in which the high-temperature melting process tends to enhance the Yb^{3+} and Ti^{4+} site disorder. Their studies revealed that generally the polycrystalline samples have better chemical stoichiometry than single crystals. For example, most studied polycrystalline samples shows a sharp anomaly in the specific heat around 0.2–0.26 K, and the single crystals usually show broad features in the specific heat with sample dependence. Recently, several μSR experiments even within polycrystalline samples yielded different results [18,19]. Therefore, despite all these intensive studies, the true nature of this unconventional magnetic ground state, or this transition around 0.26 K, in $Yb_2Ti_2O_7$ is still under debate. To clarify this controversy is of great interest and will help to better understand the QSL behavior in pyrochlores.

Moreover, how various perturbations affect this fragile QSL state has not been systematically studied. However, the studies on perturbation effects, such as the chemical pressure, are important since a thorough study of the neighborhood of $Yb_2Ti_2O_7$ in composition space should help to clarify the factors that influence the ground state. Recent studies [20–22] on $Yb_2Sn_2O_7$, with a larger lattice parameter than that of $Yb_2Ti_2O_7$, showed a ferromagnetic ordering below 0.11 K but with persistent spin dynamics down to 0.05 K, indicating it is approaching a quantum phase transition near the ferromagnetic ordered critical point. The comparison between the Sn and Ti samples already shows that the lattice parameter change or the application of chemical pressure on Yb-pyrochlores can perturb the the fragile magnetic ground state. To further probe this state, we have synthesized another pyrochlore, $Yb_2Ge_2O_7$, by using a high-temperature–high-pressure (HTHP) technique [23,24]. This sample has a smaller lattice parameter than that of $Yb_2Ti_2O_7$ due to the small ionic size of Ge^{4+}. The series of $Yb_2X_2O_7$ (X = Sn, Ti, and Ge) then provide a unique opportunity to examine how the chemical pressure consistently affects their magnetic ground states.

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Here, we use the linear and nonlinear ac susceptibility measurements on the $Yb_2X_2O_7$ series to study their magnetic ground states. Until now, the nonlinear ac susceptibility component has been largely neglected for exotic magnetism studies in pyrochlores, but we show that it can efficiently provide critical information for identifying the true character of various magnetic ground states.

Polycrystalline samples of $Yb_2Ti_2O_7$ and $Yb_2Sn_2O_7$ were made by standard solid state reactions. The ac susceptibility measurement is obtained using an ac-dc current calibrator (Valhalla Scientific, model 2700) and three lock-in amplifiers (Stanford Research, SR 830). The phases of the lock-in amplifiers are set to measure each harmonics signal, which is shifted from the oscillating magnetic field according to Eq. (2). The lock-in amplifiers are also set to read the linear component (first harmonic response) and the nonlinear components (second and third harmonic responses) with respect to the oscillating ac field frequency. The rms amplitude of the ac excitation field (h_0) varies from 0.43 to 4.3 Oe with frequency (f) ranging from 40 to 1000 Hz. The applied external dc magnetic field (H_{dc}) varies from 0 to 1000 Oe. The data were taken while warming up the sample from the base temperature with a rate of 7.6 mK/min with the zero-field-cooling process. The linear and nonlinear ac susceptibility values have been scaled by the ac field and ac frequency. The susceptibility values, therefore, can be compared for each individual sample of $Yb_2B_2O_7$.

The notations of the linear and nonlinear ac susceptibility terms are described as follows. Principally, the magnetization m is expressed as

$$m = m_0 + \chi_0 h + \chi_1 h^2 + \chi_2 h^3 + \cdots . \quad (1)$$

Then in the ac susceptibility measurements, the induced voltage E of the pick-up coil is given, applying the magnetic field $h = h_0 \sin\omega t$, as

$$E = A\{\chi_0^t h_0 \cos\omega t + \chi_1^t h_0^2 \sin 2\omega t - 3/4\chi_2^t h_0^3 \cos 3\omega t - 1/2\chi_3^t h_0^4 \sin 4\omega t + \cdots\} \quad (2)$$

with

$$\chi_0^t = \chi_0 + 3/4\chi_2 h_0^2 + 5/8\chi_4 h_0^4 + \cdots , \quad (3)$$

$$\chi_1^t h_0 = \chi_1 h_0 + \chi_3 h_0^3 + 15/16\chi_5 h_0^5 + \cdots , \quad (4)$$

$$3/4\chi_2^t h_0^2 = 3/4\chi_2 h_0^2 + 15/16\chi_4 h_0^4 + 63/64\chi_6 h_0^6 + \cdots . \quad (5)$$

Here, χ_0^t, $\chi_1^t h_0$, and $3/4\chi_2^t h_0^2$ are the first harmonic, second harmonic, and third harmonic component [25] that we have measured during the experiments. Since the used ac field h_0 is small, the first harmonic component is similar to the linear ac susceptibility ($\chi_0^t \approx \chi_0$). In the main text, we use χ_0^t to denote the linear ac susceptibility, and $\chi_1^t h_0$ and $3/4\chi_2^t h_0^2$ are the second harmonic and third harmonic component, respectively.

The ac susceptibility measured for $Yb_2Ti_2O_7$ is shown in Figs. 1 and 2. The characteristic behaviors are as follows: (i) both the real and imaginary parts of the linear ac susceptibility ($\chi_0^{t'}$ and $\chi_0^{t''}$, respectively) show a peak at $T_C = 0.25$ K with frequency $f = 40$ Hz, ac field $h_0 = 1.65$ Oe, and dc field

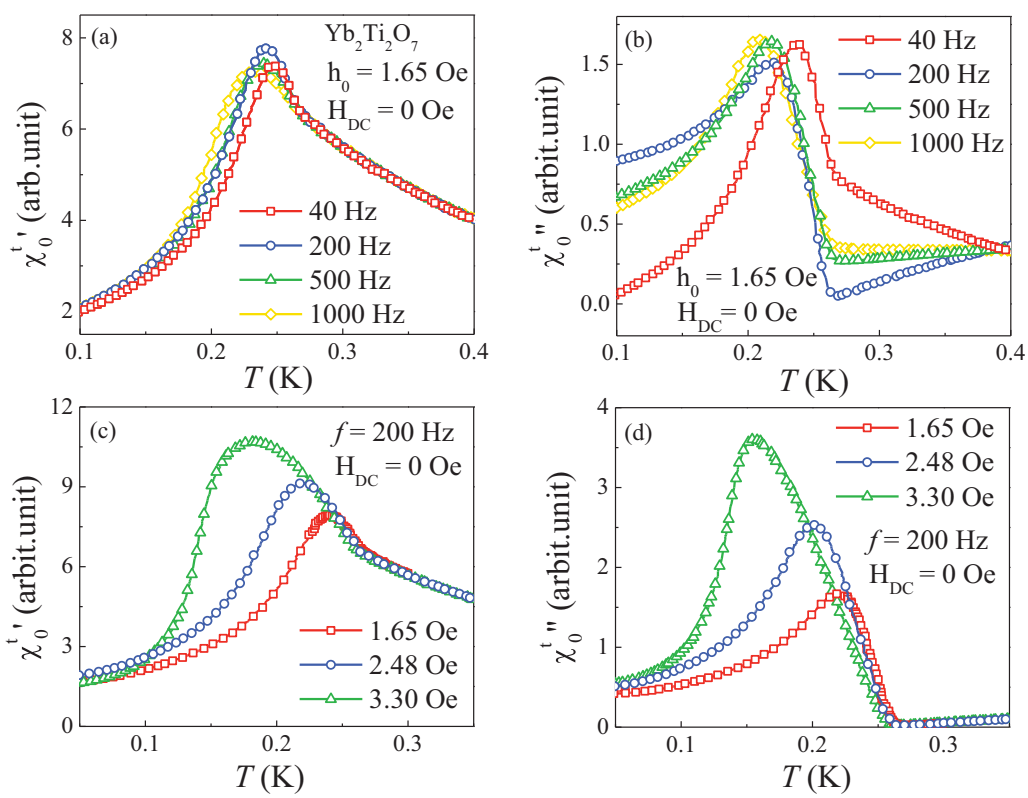

FIG. 1. (Color online) All data were taken at zero dc magnetic field ($H_{dc} = 0$ Oe) for $Yb_2Ti_2O_7$. Temperature dependencies of (a) real part $\chi_0^{t'}$ and (b) imaginary parts $\chi_0^{t''}$ of the linear ac susceptibility measured with ac field, $h_0 = 1.65$ Oe under different frequencies. Temperature dependencies of (c) $\chi_0^{t'}$ and (d) $\chi_0^{t''}$ with frequency $f = 200$ Hz under different h_0.

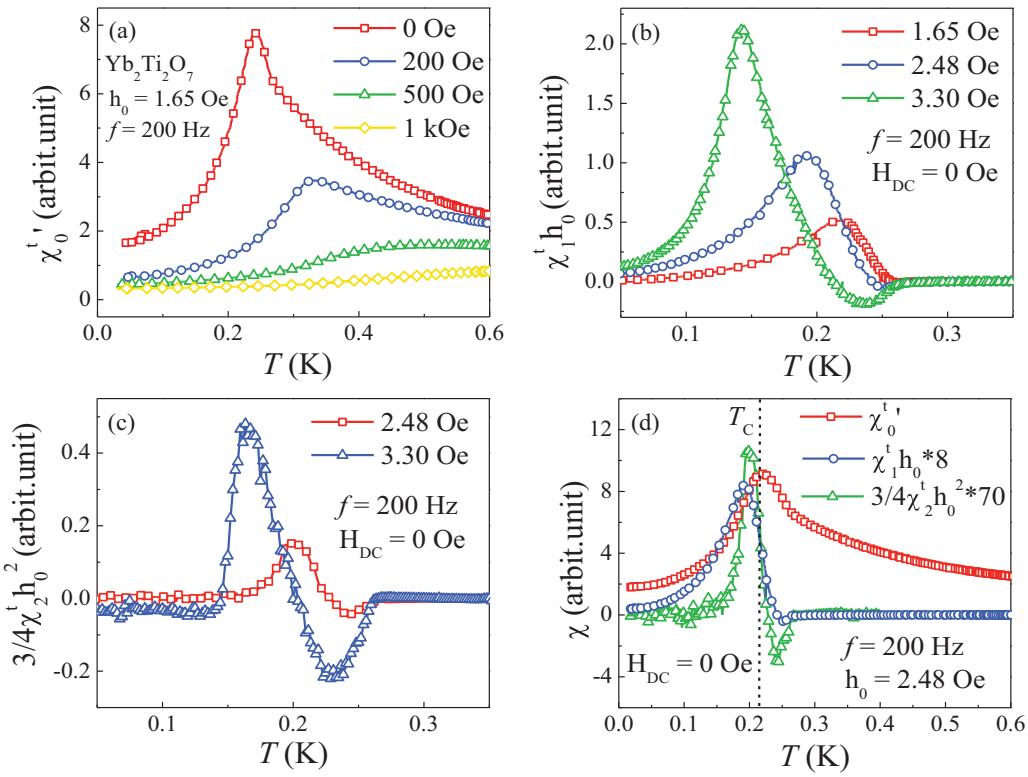

FIG. 2. (Color online) All data are for $Yb_2Ti_2O_7$. (a) Temperature dependency of $\chi_0^{t'}$ measured with $f = 200$ Hz, $h_0 = 1.65$ Oe under different H_{dc}. Temperature dependency of (b) the second harmonic component $\chi_1^t h_0$ and (c) the third harmonic component $3/4\chi_2^t h_0^2$ measured with $f = 200$ Hz, $H_{dc} = 0$ Oe under different h_0. (d) Temperature dependencies of $\chi_0^{t'}$, $\chi_1^t h_0$, and $3/4\chi_2^t h_0^2$ measured with $f = 200$ Hz, $h_0 = 2.48$ Oe, and $H_{dc} = 0$ Oe.

$H_{dc} = 0$ Oe. This result is consistent with the reported data and indicates a possible magnetic ordering at T_C [15]. With increasing f, this peak becomes broader and shifts to lower temperatures [Figs. 1(a) and 1(b)]. (ii) $\chi_0^{t''}$ is comparable to $\chi_0^{t'}$ in order of magnitude. (iii) This transition is very sensitive to the amplitude of h_0. As shown in Figs. 1(c) and 1(d), for both $\chi_0^{t'}$ and $\chi_0^{t''}$, with increasing h_0, the magnitude of the peak increases strongly and the peak shifts to lower temperatures. It is noteworthy that $\chi_0^{t'}$ is independent of h_0 above T_C but depends on h_0 at and below T_C. (iv) With increasing H_{dc}, the peak becomes broader and shifts to higher temperatures. With $H_{dc} = 1000$ Oe, the peak is almost smeared out, as plotted in Fig. 2(a). (v) The second harmonic component $\chi_1^t h_0$ plotted in Fig. 2(b) appears just below T_C (or vanishes above T_C) and shows an asymmetrical peak below T_C. (vi) The third harmonic component $3/4\chi_2^t h_0^2$ plotted in Fig. 2(c) changes its sign from negative in the region above T_C to positive in the region below T_C, when the temperature was lowered through T_C. Accordingly, the peak position of $\chi_0^{t'}$, the vanish point of $\chi_1^t h_0$, and the inflection point of $3/4\chi_2^t h_0^2$ are consistently located at T_C, as shown in Fig. 2(d).

The ac susceptibility measured for $Yb_2Sn_2O_7$ is shown in Fig. 3. Its linear ac susceptibility shows a similar peak to that of $Yb_2Ti_2O_7$, but at a lower temperature $T_C = 0.13$ K with $f = 47$ Hz, $h_0 = 1.4$ Oe, and $H_{dc} = 0$ Oe. The overall behavior of this transition for $Yb_2Sn_2O_7$, shown from the linear component under different frequency [Figs. 2(a) and 2(b)], different h_0 [Figs. 2(c) and 2(d)], different H_{dc} (Fig. 1 from Ref. [19]), and the second and third harmonic components [Figs. 2(e) and 2(f), respectively], is similar to that of $Yb_2Ti_2O_7$. One noteworthy feature is that $\chi_0^{t'}$ for $Yb_2Sn_2O_7$ [Fig. 2(c)] starts to show the dependence of h_0 below 0.4 K with increasing h_0, which is much higher than its T_C. This is different from that of $Yb_2Ti_2O_7$, in which $\chi_0^{t'}$ is independent of h_0 above T_C.

The linear ac susceptibility measurements with a fixed ac field have been intensively used to study the short-range-ordered ground states for spin ices $Dy_2Ti_2O_7$ [26,27], $Ho_2Ti_2O_7$ [28,29], spin liquid $Tb_2Ti_2O_7$ [30,31], and related $R_2Sn_2O_7$ [29,32] pyrochlores. The limited ac susceptibility data reported on $Yb_2Ti_2O_7$ show a transition around 0.24 K [15]. It is difficult to tell the exact nature of this transition from this linear ac susceptibility data. On the other hand, the linear susceptibility (χ_0^t) measured with different h_0 and the nonlinear susceptibility (second harmonic $\chi_1^t h_0$ and third harmonic $3/4\chi_2^t h_0^2$ components) resulting from hysteresis and nonlinearity of magnetization can provide critical information on the nature of magnetic phase transitions. The reported linear and nonlinear ac susceptibility studies on various magnetic materials have provided consistent evidence to identify the characteristics of different magnetic ground states [25,33–39]. For spin glasses [33,34], the $\chi_0^{t'}$ shows a symmetrical cusp at the spin-glass transition temperature (T_{SG}), which shifts to higher temperatures with increasing frequency. For ferromagnetic (FM) ordering, (i) χ_0^t, $\chi_1^t h_0$, and $3/4\chi_2^t h_0^2$ all show an asymmetrical peak at the FM transition temperature (T_C) [33]. It is important to note that $\chi_1^t h_0$ can be observed only if a

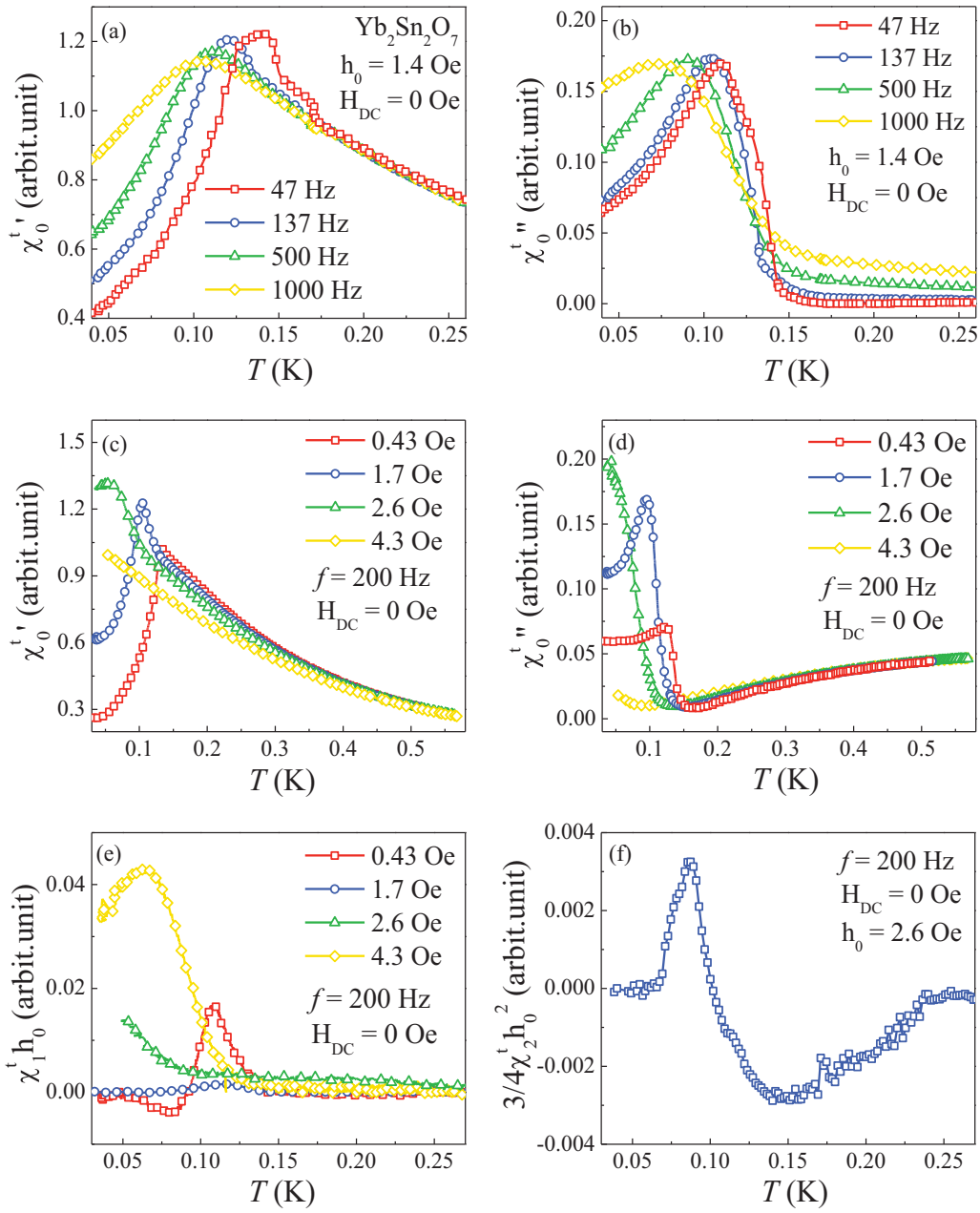

FIG. 3. (Color online) All data were taken with $H_{dc} = 0$ Oe for $Yb_2Sn_2O_7$. Temperature dependencies of (a) $\chi_0^{t\prime}$ and (b) $\chi_0^{t\prime\prime}$ measured with $h_0 = 1.4$ Oe under different frequencies. Temperature dependencies of (c) $\chi_0^{t\prime}$, (d) $\chi_0^{t\prime\prime}$, and (e) $\chi_1^t h_0$ measured with $f = 200$ Hz, $H_{dc} = 0$ Oe under different h_0 and (f) $3/4\chi_2^t h_0^2$ measured with f =200 Hz, $h_0 = 2.6$ Oe, and $H_{dc} = 0$ Oe.

system exhibits a spontaneous magnetization, due to the lack of inversion symmetry with respect to the applied ac field. Therefore, for a direct paramagnetic to spin-glass transition, only odd harmonics are expected, while for ferromagnets both even and odd harmonics should be present [25,37–39]. (ii) $\chi_0^{t\prime\prime}$ is comparable in magnitude to $\chi_0^{t\prime}$. (iii) The peak of $\chi_0^{t\prime}$ is sensitive to h_0. Normally, the peak becomes stronger and shifts to lower temperatures with increasing h_0. This is due to the contribution of domain magnetization in the FM region. This is also why $\chi_0^{t\prime}$ is just dependent on h_0 in the FM phase below T_C but shows independence of h_0 in the paramagnetic phase above T_C [25]. (iv) T_C shifts to higher temperatures with increasing H_{dc}, which is caused by superposition of an internal field and an externally applied field. (v) $\chi_1^t h_0$ vanishes above T_C and $3/4\chi_2^t h_0^2$ diverges with negative sign in the paramagnetic region above T_C. Both phenomena have been explained in the framework of molecular field theory considering the domain magnetization [25,35]. For antiferromagnetic (AFM) ordering, (i) the peak of $\chi_0^{t\prime}$ at T_N is independent of the frequency and amplitude of h_0; (ii) $\chi_0^{t\prime\prime}$ is much weaker in magnitude than $\chi_0^{t\prime}$; (iii) there is no signal for nonlinear ac susceptibility [37]; and (iv) T_N shifts to lower temperatures with increasing H_{dc}.

The characteristic behaviors of the ac susceptibility shown in Figs. 1–3 then clearly suggest that the transitions at 0.13 K for $Yb_2Sn_2O_7$ and 0.25 K for $Yb_2Ti_2O_7$ are both of a ferromagnetic nature. Several other noteworthy features are

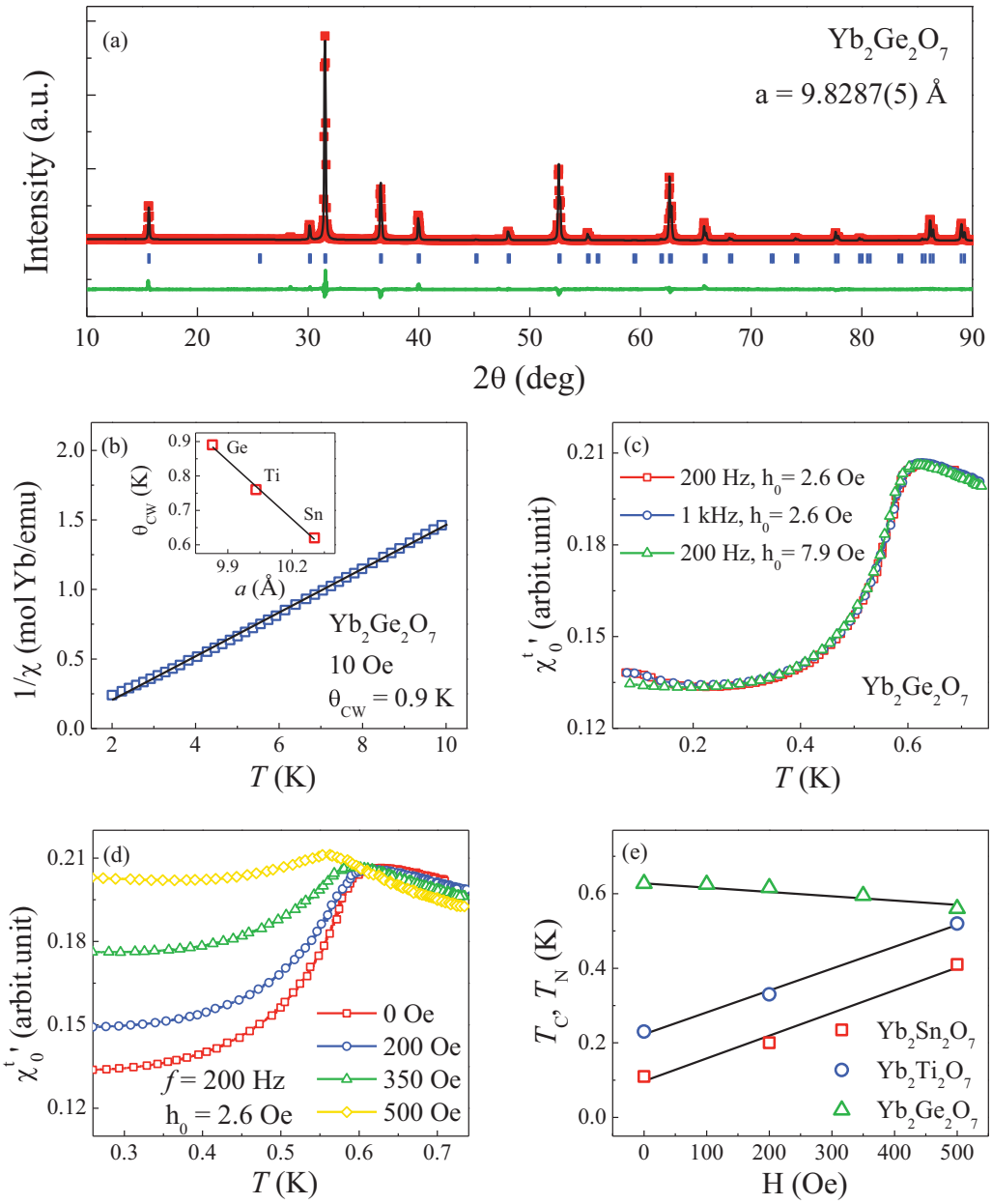

FIG. 4. (Color online) All data in (a)–(d) were taken for $Yb_2Ge_2O_7$. (a) The powder x-ray diffraction pattern of as-prepared polycrystalline samples. (b) Temperature dependency of the reciprocal susceptibility. The symbols are experimental data and the solid line is the Curie-Weiss fit. Inset: the lattice parameter dependence of the Curie constant (θ_{CW}) for $Yb_2B_2O_7$. Temperature dependency of $\chi_0^{t'}$ measured with (c) $H_{dc} = 0$ Oe under different f and h_0 and (d) $f = 200$ Hz, $h_0 = 2.6$ Oe under different H_{dc}. (e) dc magnetic field dependence of the transition temperatures for $Yb_2B_2O_7$.

as follows: (i) there is a frequency dependence for $\chi_0^{t''}$ for $Yb_2Ti_2O_7$ between 0.4 and 0.27 K [Fig. 1(b)]. Meanwhile, the neutron scattering experiments of $Yb_2Ti_2O_7$ [9] show that three-dimensional spin correlations develop below 0.4 K and then cross over to quasi-two-dimensional magnetic correlations below 0.26 K. Therefore, the frequency dependence of $\chi_0^{t''}$ observed here in the same temperature regime could be related to these three-dimensional spin correlations. (ii) There is a small shoulder above the peak at T_C for the low-frequency $\chi_0^{t'}$ and $\chi_0^{t''}$ for $Yb_2Sn_2O_7$ [Figs. 3(a) and 3(b)], which may indicate a two-step process or an inhomogeneous T_C. (iii) With increasing h_0, the $\chi_0^{t'}$ for $Yb_2Sn_2O_7$ starts to change below 0.4 K, which is higher than 0.13 K. This feature suggests that the ferromagnetic cluster, or the short-range FM ordering, already develops above T_C for $Yb_2Sn_2O_7$. This result is consistent with the recent studies on $Yb_2Sn_2O_7$ [21,22], which showed a FM ordering, but with the short-range ordering entering below 2 K and persistent spin fluctuations down to 50 mK. (iv) With increasing f, both for $Yb_2Sn_2O_7$ and $Yb_2Ti_2O_7$, the linear ac susceptibility peak shifts to lower temperatures [Figs. 1(a) and 3(a)]. Normally, for a FM transition, its ac susceptibility peak either shows no frequency dependence or shifts slightly to higher temperatures with increasing f. Future studies will be required to determine

whether this feature is intrinsic to quantum spin fluctuations or related to the recently proposed Coulombic ferromagnet [12], which is an exotic partially FM polarized phase.

The room-temperature powder x-ray diffraction pattern [Fig. 4(a)] confirms the cubic lattice for the pyrochlore $Yb_2Ge_2O_7$ prepared by the HTHP method. The obtained lattice parameter is 9.8257(5) Å, which is consistent with the reported value [40,41] and smaller than those of $Yb_2Ti_2O_7$ (a = 10.032 Å) and $Yb_2Sn_2O_7$ (a = 10.304 Å). The dc magnetic susceptibility [Fig. 4(b)] shows no magnetic ordering down to 1.8 K. The obtained Curie constant $\theta_{CW} = 0.9$ K is larger than those of $Yb_2Ti_2O_7$ ($\theta_{CW} = 0.75$ K) and $Yb_2Sn_2O_7$ ($\theta_{CW} = 0.62$ K). Here all three θ_{CW} values are consistently obtained by fitting the dc susceptibility below 10 K, which is measured at 10 Oe with the zero-field-cooling process. A general trend [inset of Fig. 2(b)] is that with the increasing lattice parameter for Yb-pyrochlores, the θ_{CW} value decreases.

The characteristic behaviors of the ac susceptibility for $Yb_2Ge_2O_7$ are as follows: (i) The $\chi_0^{t'}$ shows a peak at $T_N = 0.62$ K. This feature is independent of the amplitude and frequency of ac field [Fig. 4(c)]; (ii) $\chi_0^{t''}$ exhibits a much weaker signal than $\chi_0^{t'}$ (not shown here). (iii) No signal for nonlinear susceptibility. (iv) With increasing H_{dc}, T_N for $Yb_2Ge_2O_7$ shifts to lower temperatures [Fig. 4(d)], which is distinct from that of T_C for $Yb_2Ti_2O_7$ and $Yb_2Sn_2O_7$. Figure 4(e) shows a comparison among the dc field dependence of T_N and T_C for Yb-pyrochlores. All of these features are significantly different from those of $Yb_2Ti_2O_7$ and $Yb_2Sn_2O_7$ with FM nature. Actually, they correspond with those characteristic behaviors of an AFM ordering with $T_N = 0.62$ K.

For $Yb_2B_2O_7$, with decreasing lattice parameter, the θ_{CW} remains positive and increases. This is expected since the smaller lattice should enhance the exchange interaction and lead to larger θ_{CW}. The change of dipolar interaction here could be neglected due to the $1/r^3$ nature of the forces. Then, $Yb_2Ge_2O_7$ exhibits an AFM ordering at 0.62 K but with a positive $\theta_{CW} = 0.9$ K. One possible reason for this inconsistency is that for $Yb_2B_2O_7$, the θ_{CW} is determined by the details of the anisotropic exchange interactions. The theoretical studies on $Yb_2Ti_2O_7$ [11] have proposed that the value of θ_{CW} is a linear combination of various exchange interactions, which can be either positive or negative. The calculated sum leads to a positive θ_{CW} for $Yb_2Ti_2O_7$. Another theoretical calculation from Thompson *et al.* gave different values of the exchange interactions for $Yb_2Ti_2O_7$, but the Curie constant is consistently positive [7]. For Yb-pyrochlores, the exchange interactions are largely affected by the local environment of the Yb^{3+} ions. The large chemical pressure imposed on $Yb_2Ge_2O_7$ may significantly tune the local structure of Yb^{3+} ions from that of $Yb_2Ti_2O_7$ and $Yb_2Sn_2O_7$, although its average structure still remains cubic, so as to lead to different exchange interactions. The signs and the values of these exchange interactions may result in AFM ordering but a positive sum for the θ_{CW}. Future studies on the local structure of Yb^{3+} ions for $Yb_2Ge_2O_7$ are needed to better understand the nature of its AFM ordering.

In summary, our ac susceptibility measurements, especially the largely neglected nonlinear ac susceptibility, successfully provided additional information to the magnetic ground states of Yb-pyrochlores, which are a transition at 0.13 K with FM nature and a short-range-ordering feature for $Yb_2Sn_2O_7$, a transition at 0.25 K with FM nature for our studied polycrystalline $Yb_2Ti_2O_7$, and an AFM ordering at 0.62 K for $Yb_2Ge_2O_7$. Through these systematical results, we (i) suggested the unconventional magnetic ground state in $Yb_2Ti_2O_7$ is of FM nature; (ii) realized an AFM ground state in $Yb_2Ge_2O_7$, which provides a new playground for exotic magnetism in pyrochlores (since so far all the experimental and theoretical studies on QSLs in pyrochlores are obtained from the FM Yb-pyrochlores, future studies on this distinct AFM state will lead to broader or different insights); (iii) demonstrated that the chemical pressure can efficiently perturb the quantum spin fluctuations in Yb-pyrochlores. These findings will guide and inform a more comprehensive understanding of the QSL physics in pyrochlores.

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