Emergence of weak pyrochlore phase and signature of field induced spin ice ground state in Dy$_{2-x}$La$_x$Zr$_2$O$_7$; $x = 0, 0.15, 0.3$

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Abstract

The pyrochlore oxides Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ are well studied spin ice systems and have shown the evidences of magnetic monopole excitations. Unlike these, Dy$_2$Zr$_2$O$_7$ is reported to crystallize in a distorted fluorite structure. We present here the magnetic and heat capacity studies of La substituted Dy$_2$Zr$_2$O$_7$. Our findings suggest the absence of spin ice state in Dy$_2$Zr$_2$O$_7$ but the emergence of the magnetic field induced spin freezing near $T \approx 10$ K in ac susceptibility measurements which is similar to Dy$_2$Ti$_2$O$_7$. The magnetic heat capacity of Dy$_2$Zr$_2$O$_7$ shows a shift in the peak position from 1.2 K in zero field to higher temperatures in the magnetic field, with the corresponding decrease in the magnetic entropy. The low temperature magnetic entropy at 5 kOe field is $R \ln 2 - (1/2)R \ln (3/2)$ which is the same as for the spin ice state. Substitution of non-magnetic, isovalent La$^{3+}$ for Dy$^{3+}$ gradually induces the structural change from highly disordered fluorite to weakly ordered pyrochlore phase. The La$^{3+}$ substituted compounds with less distorted pyrochlore phase show the spin freezing at lower field which strengthens further on the application of magnetic field. Our results suggest that the spin ice state can be stabilized in Dy$_2$Zr$_2$O$_7$ either by slowing down of the spin dynamics or by strengthening the pyrochlore phase by suitable substitution in the system.

Keywords: magnetism, spin ice, pyrochlore

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Geometrically frustrated magnetic systems have been a subject of continuing research interest because of the realization of interesting quantum phases, non-trivial magnetic ordering and excitations originating from the competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions [1–6]. Of particular interest are the pyrochlore oxides: Dy$_2$Ti$_2$O$_7$, Nd$_2$Zr$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ where the exotic magnetic and thermodynamic properties have been observed at low temperature [7–10]. Pyrochlore oxide A$_2$B$_2$O$_7$, (A is the trivalent rare-earth ion and B tetravalent transition metal ion) contains a network of corner-sharing tetrahedra where the magnetic rare-earth ions reside at the corners of tetrahedra and play a major role in deciding the magnetic behavior of these systems [11, 12]. In pyrochlores, the exotic magnetic ground state is achieved by three competing interactions: AFM exchange interaction, FM dipolar interactions and crystal electric field (CEF), where the
dominant effect of CEF forces the spin to point either directly towards or away from the center of the tetrahedra and induces spin anisotropy in the system. For example, in Ho2Ti2O7 and Dy2Ti2O7 spin ice ground state is achieved by spins and their excitations are magnetic monopoles, Er2Ti2O7 has the AFM ordering which is achieved through order-by-disorder mechanism and spin liquid ground state is observed in Tb2Ti2O7 [13–16]. The computational studies on these systems have suggested the presence of spin ice state (two in–two out ordering) due to the dominance of FM dipolar interactions over the AFM exchange interactions which favors all-in–all-out ordering [17, 18].

More recently Ramon et al have shown Dy2Zr2O7 to crystallize in defect-fluorite structure with lattice constant $a = 5.238(2)$ Å [19]. Unlike Dy2Ti2O7, Dy2Zr2O7 shows the absence of spin ice state [20]. Although the specific heat and neutron scattering studies suggest very dynamic, short range, AFM spin–spin correlation below 10 K and the system remains disordered down to 40 mK with a significant value of magnetic susceptibility [19]. In Dy2Ti2O7, the spin state satisfy the two-in-two-out ice rule and possess the Pauling’s residual disorder and spin frustration at low temperature leads to the dynamic ground state of Dy2Zr2O7 [19].

Here, we present the structural, magnetic and thermodynamic properties of Dy2–xLa2xZr2O7; $x = 0, 0.15, 0.3$ based on dc magnetic susceptibility, ac magnetic susceptibility, isothermal magnetization and heat capacity measurements. It is observed that Dy2Zr2O7 is a frustrated magnetic system which undergoes spin freezing transition at $T_f \sim 10$ K in dc susceptibility measured in the presence of dc magnetic field of 5 kOe. This spin freezing transition is similar to the transition in Dy2Ti2O7 at $T = 16$ K in zero dc field, which is lost due to large structural disorder introduced by Zr atoms, and recovers on application of magnetic field. The partial substitution of non-magnetic La3+ in place of magnetic Dy3+ stabilizes the pyrochlore phase and spin–ice behavior is seen at lower fields. These results suggest that magnetic field can induce the spin-ice state in Dy2Zr2O7 and La substitution can favor spin-ice formation at even lower field.

### 2. Experimental details

The polycrystalline Dy2–xLa2xZr2O7 ($x = 0, 0.15, 0.3$) compounds were prepared by the reaction of stoichiometric mixture of constituent oxides: Dy2O3 (Sigma Aldrich, $\geq 99.99\%$ purity), La2O3 (Sigma Aldrich, $\geq 99.999\%$ purity) and ZrO2 (Sigma Aldrich, 99% purity) in the alumina crucible at 1350°C in air for 50 h [21]. The reaction at this temperature was done thrice with the intermediate grindings using an agate mortar and pestle. The Dy2O3 and La2O3 were pre-heated at 500°C to get rid of any possible moisture because of the hygroscopic nature of rare earth oxides. The obtained compounds were further pelletized and sintered at 1350°C for 50 h.

The crystal structure and phase quality of the sample was confirmed by the Rietveld refinement of the x-ray diffraction (XRD) pattern using Fullprof Sulf software. Raman spectra of the compound was obtained at 300 K in back scattering geometry by using Horiba HR-Evolution spectrometer with 532 nm excitation laser. The x-ray photoemission spectroscopy (XPS) showed the Dy and Zr atoms to exhibit +3 and +4 oxidation state respectively (shown in figure 3), similar to Dy and Ti in Dy2Ti2O7 and XPS spectrum does not show any peak corresponding to the oxygen vacancy [6]. The magnetic measurements were performed using Quantum Design built Magnetic Property Measurement System (MPMS) and heat capacity was measured using Quantum Design built Physical Property Measurement System (PPMS).

We performed DFT calculations using the projector-augmented wave (PAW) pseudopotential and a plane wave basis method as implemented in the Vienna $ab$ initio Simulation Program [22]. The exchange–correlation functional used in our calculations is Perdew–Burke–Ernzerhof generalized gradient approximation (PBE–GGA) [23]. Coulomb interaction ($U$) and spin–orbit interaction (SO) were considered within GGA + $U$ + SO approximation [24]. An energy cut-off of 500 eV was used for the plane waves in the basis set while a $5 \times 5 \times 5$ Monkhorst–Pack k-mesh centered at $\Gamma$ was used for performing the Brillouin zone integrations.

### 3. Results and discussions

#### 3.1. Crystal structure

Figure 1(a) shows the Rietveld refined XRD data of Dy2Zr2O7 at $T = 300$ K fitted with space group Fd3m. The XRD pattern consists of main peaks belonging to the pyrochlore lattice but some of the super-structural peaks corresponding to $2\theta = 14^\circ$ (111), $27^\circ$ (311), $36^\circ$ (331), $42^\circ$ (422) are missing [25]. The XRD of Dy2–xLa2xZr2O7; $x = 0.15, 0.3$ (figures 1(b) and (c)) also shows similar patterns with a slight shift in peak position towards lower angle (shown in the inset of figure 1(b)). The variation in lattice constant and position of oxygen ion $x$(O) with La substitution is plotted in the inset of figure 1(c). Recently Ramon et al has reported a good fit for Dy2Zr2O7 with Fm3m disordered fluorite space group [19]. However we have found a better fit of XRD data with Fd3m space group ($\chi^2 = 1.46$) compared to Fm3m ($\chi^2 = 1.86$).

In pyrochlore structure, 1/8 of the anion sites are vacant and these vacancies occupy a distinct site. Whereas in fluorite structure the O atoms locally form a perfect cube around the magnetic ions. The variation in $x$(O) with La substitution is plotted in the inset of figure 1(c).

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For $\chi^2_{\text{ideal}} = 0.3125$, B sites form an ideal octahedron and position of $x = 0.375$ indicates distorted octahedron for B atom.
Figure 1. X-ray diffraction pattern of Dy$_2$Zr$_2$O$_7$ collected at room temperature along with Rietveld refinement using Fd$ar{3}$m space group. Inset of figures 2(b) and (c) represents the shift in peak position, lattice constant and $x$(O) parameter with La substitution in Dy$_{2-x}$La$_x$Zr$_2$O$_7$ for $x$ = 0.0, 0.15 and 0.3. and perfect cubic symmetry for A atom. The value of $x$(O) for Dy$_2$Ti$_2$O$_7$ is 0.4243 and replacement of Ti with Zr reduces it to 0.3662 for Dy$_2$Zr$_2$O$_7$ [9]. This large variation in $x$(O) with Zr substitution expectantly changes the coordination of B site by forming the highly distorted octahedron and reduces the asymmetry around A site. The structure of Dy$_2$Zr$_2$O$_7$ is slightly equivalent to disordered fluorite with $x$ = 0.3662 ($\Delta x$ = 2.35\%). The $x$(O) position is directly related to the structure and strongly affect the $\langle$Zr–O–Zr$\rangle$ and $\langle$Dy–O–Dy$\rangle$ bond angle which are 72.41° and 109° respectively. In particular, $\langle$B–O–B$\rangle$ angle for fluorite structure is 109° and for pyrochlore structure, it increases to 120–130°. The obtained $\langle$Dy–O–Dy$\rangle$ bond angle favor the formation of pyrochlore phase and $\langle$B–O–B$\rangle$ bond angle is small but closer to the other members of pyrochlore family [29, 30].

Further the stability of pyrochlore structure can be estimated by the ratio of cationic radii ($r_A/r_B$) [31]. For pyrochlore structure, $r_A/r_B$ ranges between 1.48 to 1.78. The deviation whether smaller/larger than these values leads to the formation of defect-fluorite/perovskite type structure respectively [32]. For Dy$_2$Zr$_2$O$_7$, the $r_A/r_B$ ratio of 1.43 (where $r_A = 1.027$ Å and $r_B = 0.72$ Å for Dy$^{3+}$ and Zr$^{4+}$ respectively) indicates the formation of defect fluorite structure. On the substitution of La$^{3+}$ in Dy$_2$Zr$_2$O$_7$, the $r_A/r_B$ ratio shifted towards pyrochlore regime (see Table 1).

We have shown room temperature Raman spectra of Dy$_{2-x}$La$_x$Zr$_2$O$_7$ in Figure 2. The Raman spectrum of fluorite is known to possess a single broad band (T$_2g$) because of the random distribution of oxygen ions over the anion sites [27], whereas pyrochlore lattice exhibits six active Raman modes ($A_1g$, $E_g$, 4T$_2g$) [33, 34]. For Dy$_2$Zr$_2$O$_7$, Raman bands are observed at 123 cm$^{-1}$, 323 cm$^{-1}$, 401 cm$^{-1}$, 595 cm$^{-1}$ and 650 cm$^{-1}$. We can assign the Raman mode of Dy$_2$Zr$_2$O$_7$ at 323 cm$^{-1}$ (due to B–O$_6$ banding vibrations) to T$_{2g}$, 401 cm$^{-1}$ (mostly B–O, A–O stretching and O–B–O bending vibrations) to E$_g$ and 595 cm$^{-1}$ (mostly B–O stretching) to T$_{2g}$ [35, 36]. The single broad band at $\sim$466 cm$^{-1}$ corresponding to the fluorite structure was not observed by us [27]. A relatively weak band observed at 123 cm$^{-1}$ can be associated with disorder in the system or anharmonic effect [35] and band at 650 cm$^{-1}$ can be attributed to the higher coordination of B site [37].

Thus, it can be inferred that although a substantial global disorder is seen from XRD measurements, ordering at microdomains seen from Raman spectra favors the weak pyrochlore structure in bulk. Based on x-ray, Raman and synchrotron radiation XRD techniques Mandal et al have shown that Dy$_2$Hf$_2$O$_7$

| Table 1. Crystallographic data and magnetic parameters of Dy$_{2-x}$La$_x$Zr$_2$O$_7$; $x$ = 0, 0.15, 0.3. |
|---|---|---|
| $x$ | $a$ (Å) | $r_A/r_B$ | $x$(O) | $\chi^2$ | $\mu_{eff}$ ($\mu_B$) | $\theta_{cw}$ ($K$) | $J_{obs}/D_{inc}$ |
| 0 | 10.4511(3) | 1.43 | 0.3662 | 1.46 | 8.20 | -9.6 (2) | -0.86 |
| 0.15 | 10.4832(4) | 1.44 | 0.3674 | 2.26 | 7.99 | -7.91 (2) | -0.863 |
| 0.3 | 10.4972(3) | 1.45 | 0.3692 | 2.22 | 7.06 | -7.14 (1) | -0.87 |

Figure 2. Room temperature Raman spectra of Dy$_{2-x}$La$_x$Zr$_2$O$_7$; $x$ = 0, 0.15 and 0.3, showing the presence of Raman modes corresponding to pyrochlore structure.
is a weakly ordered pyrochlore which possess remnants of pyrochlore in Raman spectra and presence of superstructure peaks in the XRD [25].

Upon substitution of La, all the five pyrochlore Raman modes become sharp and intense. Additionally, La substituted compounds shows one extra peak at 512 cm\(^{-1}\) which is marked as A\(_{2g}\). This mode has particular importance in pyrochlores as it is directly related to the trigonal distortion of B-O\(_6\) octahedra through the modification of \(<\text{B–O–B}\>\) bond angle [38]. These results suggest that the structural symmetry increases with substitution and leads the system towards weakly ordered pyrochlore phase.

The x-ray photoemission spectroscopy (XPS) measurement on Dy\(_2\)Zr\(_2\)O\(_7\) (figure 3) confirmed +3 and +4 oxidation state of Dy and Zr ion as that of Dy and Ti in Dy\(_2\)Ti\(_2\)O\(_7\) [21]. The XPS spectra of oxygen contains two signals. The first signal (O-1s) at ~529 eV corresponds to lattice oxygen and a very weak signal (marked by star) at ~532 eV indicates defects/vacancies or surface chemically absorbed oxygen [39]. The ordered oxygen vacancies of the pyrochlores might be the possible reason for the observation of a weak signal at ~532 eV.

3.2. DC magnetization

DC magnetization of the compounds (figure 4) was measured in the temperature range \(T = 1.8\) K–300 K in zero field cooled (ZFC) and field cooled (FC) protocol at the magnetic field \(H\) of 5 kOe. Similar to Dy\(_2\)Ti\(_2\)O\(_7\), dc susceptibility \(\chi_{\text{dc}}(T)\) of Dy\(_2\)–La\(_x\)Zr\(_2\)O\(_7\) increases monotonically on cooling and does not show any anomaly down to 1.8 K [9]. Interestingly, \(\chi_{\text{dc}}(T)\) shows lowering in the value below 15 K for the high fields of \(H = 10\) kOe and 20 kOe (right inset of figure 4) and indicates the development of magnetic spin correlation for \(T \leq 15\) K. However, the absence of thermal hysteresis between ZFC and FC curves rules out the formation of magnetic cluster or spin glass like freezing at this temperature in these compounds.

The Curie–Weiss \(\chi = C/(T - \theta_{\text{CW}})\) fit of \(\chi^{-1}(T)\) data for Dy\(_2\)Zr\(_2\)O\(_7\) in the temperature above 30 K (left inset of figure 4) gives \(\theta_{\text{CW}} = -9.6(2)\) K, \(\mu_{\text{eff}} = 16.41\) \(\mu_B\) and the same fitting in the low temperature range below 30 K yields \(\theta_{\text{CW}} = -1.9(4)\) K. With the inclusion of the correction for demagnetization factor for powdered compound, the readjusted \(\theta_{\text{CW}}\) values are \(-8.1(2)\) K and \(-0.5(4)\) K for the mentioned temperature ranges, which indicate AFM interactions between

\[
\frac{D_{\text{nn}}}{\mu_0} = \frac{3}{5} \frac{(\mu_0)}{4\pi} \frac{\mu_{\text{eff}}^2}{r_{\text{nn}}}
\]

Using the distance between nearest neighbor Dy\(^{3+}\) ions, \(r_{\text{nn}} = (a/4\sqrt{2}) = 3.70\) Å \((a = \text{lattice constant})\) and \(\mu_{\text{eff}} = 8.20\) \(\mu_B\), we obtained \(D_{\text{nn}} = 1.38\) K for Dy\(_2\)Zr\(_2\)O\(_7\). To determine the nearest neighbor exchange interactions \(J_{\text{nn}}\), the \(\chi_{\text{dc}}(T)\) data was fitted by \(\chi_{\text{dc}}(T) = (C_1/T)(1 + C_2/T)\), where \(C_1\) is the Curie constant and \(C_2\) consists of the exchange and dipolar terms between the \(\langle 111 \rangle\) Ising moments \((C_2 = (6S^2/4)(2.18D_{\text{nn}} + 2.67D_{\text{nn}}))\) in the linear low temperature region 10 K–30 K [11]. The fitting yields \(C_2 = -1.55(03)\) and using \(D_{\text{nn}} = 1.38\) K, we obtained \(J_{\text{nn}} = -1.188\) K. The ratio \(J_{\text{nn}}/D_{\text{nn}} = -0.86\) is close to the value for spin ice (–0.91), and thus favors the spin ice behavior [43]. Byron et al has explained the occurrence of spin ice behavior in Dy\(_2\)Ti\(_2\)O\(_7\) and Ho\(_3\)Ti\(_2\)O\(_7\) despite the presence of long-range dipolar interactions and showed that the spin ice behavior is recovered over a large range of \(J_{\text{nn}}/D_{\text{nn}}\) parameter [43]. The \(J_{\text{nn}}/D_{\text{nn}}\) ratio for these spin ice candidates are –0.53 and –0.22 respectively [8].

![Figure 3](image-url) XPS spectra of Dy, Zr and O ions of Dy\(_2\)Zr\(_2\)O\(_7\) collected at room temperature.

![Figure 4](image-url) DC magnetic susceptibility \(\chi_{\text{dc}}\) versus \(T\) at \(H = 5\) kOe for Dy\(_2\)–La\(_x\)Zr\(_2\)O\(_7\). Inset (left): Curie–Weiss fitting (red line) of \(\chi^{-1}(T)\) in \(30 \leq T \leq 300\) K at \(H = 5\) kOe. Inset (right): \(\chi_{\text{dc}}(T)\) versus \(T\) at \(H = 10\) kOe and 20 kOe for Dy\(_2\)Zr\(_2\)O\(_7\).
The $J_{nn}/D_{nn}$ ratio increases with La substitution (see table 1) and is expected to stabilize the spin ice phase in the substituted compounds.

In order to determine an accurate value of the ratio $J_{nn}/D_{nn}$, we have estimated the nearest neighbor Dy–Dy exchange interaction $J_{nn}$ from first principles DFT calculations for the parent compound Dy$_2$Zr$_2$O$_7$. $J_{nn}$ was calculated by mapping the total energy difference to a classical Heisenberg spin Hamiltonian [44]. We considered four different spin configurations of two neighboring Dy$^{3+}$ spins: (i) $\uparrow \uparrow$, (ii) $\downarrow \downarrow$, (iii) $\uparrow \downarrow$ and (iv) $\downarrow \uparrow$ with corresponding total energies given by $E_1$, $E_2$, $E_3$ and $E_4$ respectively keeping all other spins ferromagnetically aligned. The $J_{nn}$ is then calculated by following formula

$$J_{nn} = (E_1 + E_2 - E_3 - E_4)/4nS^2$$

where $S = 15/2$, $n = 2$. The calculated nearest neighbor exchange interaction within GGA + SO approximation is found to be AFM in nature and the value is $-1.276$ K. For this value of $J_{nn}$, we obtain the ratio $J_{nn}/D_{nn}$ to be $-0.92$ which lies in the range of spin ice systems [43]. Thus, our results substantiates the possibility of spin ice behavior for Dy$_2$Zr$_2$O$_7$. It is to mention that even without the application of Coulomb correlation $U$, we obtain magnetic moment value at Dy site to be $4.9\mu_B$ with the value of $J_{nn}/D_{nn}$ to be $-0.92$ for $U_{eff} = 0$ being the closest to the spin ice value.

The isothermal $M(H)$ for Dy$_{2-x}$La$_x$Zr$_2$O$_7$ measured at $T = 5$ K are shown in figure 5. Initially $M$ increases rapidly with field and tends towards saturation above $H \geq 30$ kOe in the substituted compounds only. The saturation magnetization ($M_s$) value of 4.80 $\mu_B$/Dy for Dy$_2$Zr$_2$O$_7$ at 70 kOe is close to $M_s = 5\mu_B$/Dy for Dy$_2$Ti$_2$O$_7$ [45]. These values are $\sim 45\%$ lower than the free ion theoretical value of $M_s = 10.64\mu_B$/Dy, and indicate the strong Ising anisotropy similar to a local $<111>$ Ising anisotropic system [9, 10]. The $M_s$/Dy values decrease further for the La substituted Dy$_2$Zr$_2$O$_7$. The reduction in $M_s$/Dy ($\sim 4–25\%$) in comparison to Dy$_2$Ti$_2$O$_7$ points to enhanced anisotropy in Dy$_2$Zr$_2$O$_7$ compounds [45]. It is to note that $M(H)$ value (at $T = 5$ K) reaches to saturation state value of $<M> = 3.33\mu_B$/Dy, for the field of $H \approx 10–20$ kOe only, which is in line to the ice rule along $[111]$ axis. For higher fields, magnetization saturates ($M_s = 4.80\mu_B$/Dy) for Dy$_2$Zr$_2$O$_7$ in accordance with the three-in-one-out configuration $g_{zz}(1 + (1/3) \times 3)/4 = 5\mu_B$/Dy [9]. This large value of magnetization along $[111]$ axis compared to the ice rule expected value (3.33 $\mu_B$/Dy) confirms the presence of strong Ising anisotropy in the system which results in the breakdown of ice rule [9]. The magnetization does not reach to the saturating value up to 70 kOe in Dy$_2$Zr$_2$O$_7$, whereas in La substituted Dy$_2$Zr$_2$O$_7$ saturation is attained at lower field that indicate the reduction in disorder in the substituted compounds and favor the stabilization of pyrochlore phase on La substitution.

Considering the effective spin half doublet ground state system with local $<111>$ Ising anisotropy with transverse and longitudinal $g$-factors ($g_\perp = 0$ and $g_\parallel = g_{zz}$), the average magnetization of system is given by

$$<M> = \frac{(k_B)^2}{g_{zz}\mu_B}H^2S \int \frac{e^{\frac{x\mu_BHS}{k_B}}}{x} \tanh(x) \, dx$$

where $x = g_{zz}\mu_BHS/k_BT$. The $M(H)$ data shows a good fit with above expression for Dy$_2$Zr$_2$O$_7$ at lower field only. The fitting improves for higher temperature isotherms (see inset of figure 5) and La substituted compounds. The obtained value of $g_{zz} = 18.05(2)$ for Dy$_2$Zr$_2$O$_7$ at 5 K is close to the $g_{zz} = 2g_{\mu_B}/J = 20$, as expected for the pure Kramers doublet $m_f = \pm 1/2$ states of Dy$^{3+}$. A closer value of $g_{zz} = 18.5(1)$ is reported for Dy$_2$Ti$_2$O$_7$ in reference [40]. The value of the ground state moment of Dy $\sim 9.01(2)\mu_B$/Dy for Dy$_2$Zr$_2$O$_7$ (calculated using $m_f = g_{zz}/\mu_B$) is consistent with the $\mu_{eff}$ determined from the dc magnetization. The $g_{zz}$ value increases from $\sim 16$ at 1.8 K to $\sim 18.4$ at 7 K for Dy$_2$Zr$_2$O$_7$, and indicates the admixture of additional terms in the $m_f$. The lowering of $g_{zz}$ in La substituted compounds further points towards the enhanced anisotropy. The poor fitting of the $M(H)$ data at low temperature and high field using the spin 1/2 Ising model highlights the need for additional anisotropic terms and non-zero transverse $g$-factor in the model for these compounds. These data indicate that Dy$_2$Zr$_2$O$_7$ has dominant AFM coupling between nearest-neighbor Dy ions and easy axis anisotropy.

### 3.3. AC susceptibility

Figure 6(a) shows the temperature dependence of ac susceptibility $\chi''(T)$ of Dy$_2$Zr$_2$O$_7$ measured at different frequencies between 10–1000 Hz at zero applied dc field. The real part of ac susceptibility ($\chi'$) of Dy$_2$Zr$_2$O$_7$ (figure 6(a)) measured in zero dc magnetic field does not show any anomaly down to 1.8 K. The large value of $\chi'$ suggests the liquid like dynamic state of the system at low temperature which has been studied in detail by Ramon et al [19]. We measured $\chi''$ in the presence of dc field also. The $\chi''(T)$ measured at $H = 931$ Hz at $H = 3–30$ kOe is shown in figure 6(b). The $\chi''(T)$ is similar to zero field data,
up to 3 kOe field, however a weak anomaly starts developing near $T \approx 10$ K for $H = 5$ kOe field. The deviation in $\chi'$ from paramagnetic-like behavior leads to a sharp rise in $\chi''_{o}$ at the freezing temperature, which increases with frequency. For the further increase in field, the anomaly becomes more prominent and is pushed towards higher temperature with significant decrease in magnitude above 10 kOe. The slowing down of spin dynamics on the application of field for $T < T_{f}$ reveals magnetic spin freezing similar to the spin ice compounds: Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ [6, 7, 13]. A closer value of $\chi''_{o}$ depicts the width of $\alpha$ degree of freedom, we have quantified the frequency dependence of ac susceptibility is not seen for Dy$_2$Zr$_2$O$_7$ at higher field (7 kOe). Although there is slight increase in $\chi''_{o}$ value with increase in frequency near this anomaly, we do not observe any frequency dependence, ruling out the possibility of magnetic clustering, consistent with dc magnetization studies. [See supplementary information figure S3 (https://stacks.iop.org/JPhysCM/32/365804/mmedia)].

In order to examine the nature of spin freezing transition, we performed the $\chi_{ac}(T)$ measurement at $H = 5$ kOe for different frequencies between 10 Hz to 1000 Hz (shown in figures 6(c) and (d)). As seen from the figures, a clear anomaly is present in $\chi'(T)$ and $\chi''(T)$ below $\sim 15$ K at 13 Hz frequency. For the further increase in frequency, maximum in $\chi''(T)$ shift toward higher temperature. This feature is a signature of glassy transition in systems, having competing interactions or structural defects. To analyze the glass-like freezing of the spin degree of freedom, we have quantified the frequency dependence using the relation $p = \Delta T_{f}/T_{f}(\log f_{0})$. The obtained value of $p \approx 0.08$, is much higher than the typical spin glass ($p \approx 0.01$) [21]. The rise in freezing temperature with field also rules out the possibility of spin glass like freezing, where the application of magnetic field suppress the freezing temperature in spin glass.

The more striking difference between the glassy freezing and spin-ice freezing is found in the distribution of relaxation times. We have performed Cole–Cole analysis of $\chi''$ and $\chi'$ data as shown in the inset of figure 6(d). The Cole–Cole plot gives the distribution of relaxation times of spin-freezing process and depicts the spin dynamics at a given temperature. The $\chi''$ and $\chi'$ data is fitted within the Cole–Cole formalism, given by equation [46]

\[
\chi''(\chi') = -\frac{\chi_0 - \chi_s}{2 \tan \left( \frac{1 - \alpha}{2} \right)} + \sqrt{\left( \chi' - \chi_s \right) \left( \chi_0 - \chi_s \right) \frac{(\chi_0 - \chi_s)^2 + 4 \tan^2 \left( \frac{1 - \alpha}{2} \right)}{4 \tan^2 \left( \frac{1 - \alpha}{2} \right)}}.
\]

Here $\chi_0$ and $\chi_s$ are the isothermal and adiabatic susceptibility respectively. The parameter $\alpha$ depicts the width of the distribution of relaxation times, for single spin relaxation $\alpha = 0$. From the best fit of $\chi''$ using equation (4), we obtained $(1 - \alpha)/\pi/2 = 89.88(1)^{\circ}$. Accordingly, we obtain $\alpha \approx 0.001$, a very close value of the theoretically expected semicircle. The extremely low value of $\alpha$ and semi-circular character of the plot similar to Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ indicating the single spin relaxation or narrow distribution of relaxation time [6, 7, 13]. This is unlike the magnetic systems exhibiting glass-like behavior, where the relaxation time is typically of several orders [47–49].

Figures 7(a) and (b) show the real and imaginary part of $\chi_{ac}(T)$ of Dy$_{2-x}$La$_x$Zr$_2$O$_7$ for $x = 0.0, 0.15$ and 0.3 measured at $H = 5$ kOe. Similar to parent compound Dy$_2$Zr$_2$O$_7$, spin freezing anomaly is clearly visible in substituted compounds. These results are in agreement with the Raman spectroscopy studies insisting the strengthening of pyrochlore phase upon La substitution. As shown in the inset of figure 7(b), the spin freezing anomaly develops at lower field $H = 3$ kOe for Dy$_{1.5}$Sr$_{0.5}$Zr$_2$O$_7$ compared to Dy$_2$Zr$_2$O$_7$ ($H = 5$ kOe). Similar studies on Ca or Y substituted Dy$_2$Ti$_2$O$_7$ show suppression in the freezing transition [6, 9]. However, in the present case, non-magnetic La substitution stabilizes the pyrochlore phase and thus the spin ice state in the weakly ordered pyrochlore Dy$_{2-x}$La$_x$Zr$_2$O$_7$ system. Further the frequency dependence of ac susceptibility is not seen for Dy$_2$Zr$_2$O$_7$ at higher field (7 kOe). Although there is slight increase in $\chi'$ value with increase in frequency near this anomaly, we do not observe any frequency dependence, ruling out the possibility of magnetic clustering, consistent with dc magnetization studies. [See supplementary information figure S3 (https://stacks.iop.org/JPhysCM/32/365804/mmedia)].

3.4. Heat capacity

Figure 8 displays the magnetic contribution of the heat capacity ($C_{mag}$) of Dy$_2$Zr$_2$O$_7$ for $H = 0$–50 kOe. The $C_{mag}(T)$ was calculated from total heat capacity $C_{p}(T)$ after subtracting the lattice heat capacity. For the determination of lattice heat capacity, $C_{p}(T)$ was fitted using Debye and Einstein models (see supplementary information figure S4). The $C_{mag}(T)$ plotted on logarithmic $T$ scale shows a peak at 1.2 K at $H = 0$. We have shown the data of Ramon et al for the comparison [19]. Low temperature $C_{p}(T)$ at $H = 0$ and 50 kOe field is shown in left inset of figure 8. As seen from the figure 8, the $C_{mag}$ peak shifts towards higher temperature on the application of magnetic field and a similar behavior has been reported for Dy$_2$Ti$_2$O$_7$, Pr$_2$Zr$_2$O$_7$, Yb$_2$Ti$_2$O$_7$ etc [50–55]. It is to mention that Pr$_2$Zr$_2$O$_7$ does not exhibit any signature of long-range ordering in heat capacity and magnetic susceptibility measurements but still shows the evidence of spin correlation and quantum fluctuations [52, 56]. These results are interpreted as the indication of ice rule satisfied within the time scale of the measurements.

The magnetic entropy ($\Delta S_{m}$) of Dy$_2$Zr$_2$O$_7$ for $H = 0$ and 5 kOe is shown in the right inset of figure 8. The low temperature $\Delta S_{m}$ value of Dy$_2$Zr$_2$O$_7$ at zero field is close to $R \ln 2$ (5.76 J mol$^{-1}$ K$^{-1}$) which corresponds to the molar entropy of the classical system of two spin orientations per degree of freedom. The $\Delta S_{m}$ value decreases for higher fields and shows a remnant value of $\sim R \ln 2 - (1/2)R \ln(3/2)$ (4.07 J mol$^{-1}$ K$^{-1}$) for 5 kOe field, which is equivalent to the entropy of water ice [57, 58] and other spin ice systems Dy$_2$Ti$_2$O$_7$, Ho$_2$Ti$_2$O$_7$ [8, 20]. This is quite remarkable as the slowing down of the spin dynamics under external magnetic field leads to the spin ice state. For higher field $\Delta S_{m}$ decreases further and almost no magnetic entropy is left for $H \geq 50$ kOe. These results are consistent with the field induced spin freezing transition observed in ac susceptibility data at $H = 5$ kOe.
Figure 6. (a) The $\chi'(T)$ of Dy$_2$Zr$_2$O$_7$ measured at $H = 0$ Oe for frequencies $f = 10$ Hz to 1 kHz. (b) $T$ dependence of $\chi'$ at $f = 931$ Hz measured at different fields between $H = 3$ kOe to 30 kOe. Figures 6(c) and (d) shows the $\chi'(T)$ and $\chi''(T)$ of Dy$_2$Zr$_2$O$_7$ measured at different frequencies between 10 Hz to 1 kHz and $H = 5$ kOe. Inset of 6(c) and 6(d) are the frequency dependence of freezing temperature and Cole–Cole fit (at $T = 7.5$ K) respectively.

Figure 7. $\chi'(T)$ and $\chi''(T)$ of Dy$_2$$_{1-x}$La$_x$Zr$_2$O$_7$; $x = 0.0, 0.15, 0.3$ measured at $f = 931$ Hz and $H = 5$ kOe. Inset of 7(b) is the $\chi'(T)$ of Dy$_{1.85}$La$_{0.15}$Zr$_2$O$_7$ at $H = 3$ kOe.

Figure 8. The $C_{\text{mag}}(T)$ of Dy$_2$Zr$_2$O$_7$ for $0.4 \leq T \leq 30$ K measured at 0–50 kOe. The $C_{\text{mag}}(T)$ data from reference [19] is also shown for the comparison. Left inset shows the total heat capacity for Dy$_2$Zr$_2$O$_7$ at $H = 0$, 50 kOe. Right inset shows the recovered magnetic entropy as a function of temperature for Dy$_2$Zr$_2$O$_7$ at $H = 0$, 5 kOe. The dashed line denotes the expected entropy value for Ising spins and spin ice systems.

The dilution of Dy$_2$Zr$_2$O$_7$ with non-magnetic La shows no significant change in heat capacity behavior except the shift of the spin freezing transition towards low temperatures (see figure 9). It is reported that the substitution of 10% Ca$^{2+}$ for Dy$^{3+}$ in Dy$_2$Ti$_2$O$_7$ does not change the spin freezing transition [9]. Furthermore, similar to field dependence in Dy$_2$Zr$_2$O$_7$, the application of dc magnetic field (shown in the inset of figure 9 for $H = 20$ kOe) shifts the transition towards higher temperature for the La substituted compounds. Thus, the dilution of magnetism in Dy$_2$Zr$_2$O$_7$ by La substitution suppress the freezing transition whereas the dc magnetic field shifts the transition towards higher temperature.

4. Conclusion

Our study explores the possibility of the spin ice phase in the highly disordered fluorite/pyrochlore compound Dy$_2$Zr$_2$O$_7$. The field dependent ac susceptibility studies suggest that the Dy$_2$Ti$_2$O$_7$ like spin ice phase can be induced in Dy$_2$Zr$_2$O$_7$ by quenching the structural disorder under well controlled magnetic field. The ac susceptibility measurements in dc applied
field show the emergence of magnetic correlation/freezing near $T \sim 10$ K which is akin to that observed for Dy$_2$Ti$_2$O$_7$. Semi-circular behavior of Cole–Cole plot and a reduced value of $\alpha$ suggests the presence of single spin relaxation. Further, the ratio of antiferromagnetic interactions and dipole–dipole ferromagnetic interaction $J_{nn}/D_{nn} \sim 0.86$ favors the spin ice state in the compound. As noticed in reference [59] for Dy$_2$Ti$_2$O$_7$, the field induced magnetic transition is governed by the long-range dipolar interactions over the nearest neighbors. Similarly, in case of Dy$_2$Zr$_2$O$_7$, the $J_{eff} = J_{nn} + D_{nn}$ is large enough to favor the dominance of magnetic dipole–dipole interaction term. The smaller value of magnetic moment $\sim 8.2$ $\mu_B$/Dy in comparison to expected 10.64 $\mu_B$/Dy; and saturation magnetization $\sim 4.8$ $\mu_B$/Dy suggests strong Ising anisotropic nature of magnetic ground state.

The La substitution into Dy$_2$Zr$_2$O$_7$ stabilizes the weakly ordered pyrochlore structure, and strengthens the spin ice phase at even lower fields than required for Dy$_2$Zr$_2$O$_7$. Heat capacity results shows zero residual entropy at $H = 0$ Oe and presence of residual entropy of $R/2\ln(3/2)$ at $H = 5$ kOe indicating the stabilization of the spin ice state. On application of high magnetic field, the magnetic entropy of the system evolves from spin liquid state to water ice state and back to the non-magnetic ground state. It would be quite interesting to perform the field dependent inelastic neutron scattering study to understand the dynamics of spin to ascertain the true magnetic state of these compounds.

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