The Complex Magnetism in the Breathing Pyrochlore LiIn(Cr$_{1-x}$Rh$_x$)$_4$O$_8$ *

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We perform a detailed investigation of the new 'breathing' pyrochlore compound LiInCr$_4$O$_8$ through Rh substitution with measurements of magnetic susceptibility, specific heat, and x-ray powder diffraction. The antiferromagnetic phase of LiInCr$_4$O$_8$ is found to be slowly suppressed with increasing Rh up to the critical concentration of $x = 0.1$ where the antiferromagnetic phase is still observed with the peak in specific heat $T_p = 12.5$ K, slightly lower than $T_c = 14.3$ K for the $x = 0$ compound. From the measurements of magnetization we also uncover evidence that substitution increases the amount of frustration. Comparisons are made with the LiGa$_{1-x}$In$_{1+x}$Cr$_4$O$_8$ system as well as other frustrated pyrochlore-related materials and comparable amounts of frustration are found. The results of this work show that the engineered breathing pyrochlores present an important method to further understand the complex magnetism in frustrated systems.

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Magnetic frustration has recently attracted renewed interest as novel and exotic new phases, which can arise from the frustrated magnetic interactions.\textsuperscript{[1]} The pyrochlore class of materials is an ideal family to investigate as its crystal structure promotes magnetic frustration. \textsuperscript{[2]} Forming conventionally in the $A_2B_2O_7$ composition, the $A$ and $B$ atoms form corner-sharing tetrahedra. If the nearest neighbor exchange interactions for the $A$ and $B$ atoms are antiferromagnetic, then there are no configurations for which the magnetic moments can simultaneously satisfy all nearest-neighbor interactions, geometrically promoting magnetic frustration. It is not surprising that the pyrochlores have displayed a wide range of interesting phenomena such as spin ice and spin glasses,\textsuperscript{[3,4]} metal-insulator transitions,\textsuperscript{[5]} potential topological insulators,\textsuperscript{[6]} and superconductivity.\textsuperscript{[7-8]}

The pyrochlore family has been known for a long time, first discovered in the 1930s.\textsuperscript{[9]} However, it was only after the discovery of spin-glass-like properties in $Y_2Mo_2O_7$ did the family’s unique potential for novel magnetic properties become realized.\textsuperscript{[10]} Recently there have been several new exotic entries into the pyrochlore family. Discovered in 2015, the $RE_3Sb_3Zn_2O_{14}$ branch was the first member to display the 2D kagome lattice,\textsuperscript{[11]} which has a high potential for exhibiting the spin-liquid state. Another recent discovery was the ‘breathing’ pyrochlores and will be the focus of this work.

The breathing pyrochlores were discovered in 2013 and the first materials formed in the chemical composition $LiMCr_4O_8$, $M=In$ or Ga,\textsuperscript{[2]} a variant of the conventional pyrochlore structure. The $Li$ and $M$ atoms alternate in series and due to the large differences in size produce a lattice that periodically expands and contracts, the origin of the breathing term. Investigations on $LiMCr_4O_8$ ($M=In$ or Ga) reveal unusual magnetic and electronic properties where both compounds show a magnetic phase transition tied to structural distortions at 13.8 K and 15.9 K for $M=Ga$ and In, respectively.\textsuperscript{[12]} Nuclear magnetic resonance reveals a more complicated phase diagram with spin-gap, structural, and a long range magnetic order in LiInCr$_4$O$_8$ while LiGaCr$_4$O$_8$ shows no spin-gap but a potential tri-critical point.\textsuperscript{[13]} A more recent investigation by using multiple spin resonance techniques (electron, nuclear, and muon) shows that LiGa$_{1-x}$Cr$_4$O$_8$ has a magnetic structural phase transition at 15.2 K followed by the long-range magnetic order at 12.9 K while LiIn$_{1-x}$Cr$_4$O$_8$ crosses over from a correlated paramagnet with a weak magnetostuctural transition at 17.6 K and a long range magnetic order at 13.7 K.\textsuperscript{[14]} Furthermore, a spin-glass like phase develops in LiGa$_{1-x}$In$_{1+y}$Cr$_4$O$_8$ at moderate substitutions after the antiferromagnetism of each end member is suppressed as well as a ‘pseudo’ spin-gap behavior observed near the critical concentration of $y = 0.1$.\textsuperscript{[15]}

The pseudo spin gap behavior is observed with small Ga substitution from the LiInCr$_4$O$_8$ parent when the antiferromagnetic phase is fully suppressed. Therefore, we have performed chemical substitution of LiIn$_{1-y}$Cr$_4$O$_8$ with Rh substituted on the $Cr$ site as LiInRh$_{4-y}$O$_8$ is reported to be non-magnetic.\textsuperscript{[15]} We find that the peak $T_p$ in specific heat due to the antiferromagnetic phase is slowly suppressed with increasing Rh up to $x = 0.1$, an unexpected result as Rh substitution should significantly alter the electronic configuration. Furthermore we find evidence that the frustration is enhanced with chemical substitution and comparisons are made to other frustrated systems. We find that the frustration generated from the engineered breathing pyrochlores is comparable with the conventional geometrically frustrated systems such as ZnCr$_2$O$_4$,\textsuperscript{[13,16]} providing an important route for further understanding the complex magnetism in frustrated systems.

Polycrystalline samples of LiIn(Cr$_{1-x}$Rh$_x$)$_4$O$_8$ with $x = 0, 0.025, 0.5, 0.075, 0.1$ were synthesi-
ized by solid state reaction in a conventional Lindberg box furnace. The starting constituent materials are Li$_2$CO$_3$, In$_2$O$_3$, and Cr$_2$O$_3$/Rh$_2$O$_3$, which were dried over night at 120°C and then weighed out to the molar ratio of 1:1:4. The starting materials were then mechanically mixed, pressed into pellets, and sintered for 48h at 1100°C. After heating the samples were crushed into powder, re-pressed into pellets, and sintered up to four more times to ensure homogeneity. Powder x-ray diffraction measurements were performed on all samples by using a Bruker D8 Discover x-ray diffractometer with a Cu Kα source. Magnetization measurements were performed by using a Quantum Design vibrating magnetometer from 300K down to 2 K in applied magnetic fields up to 5 T. Specific heat measurements were performed in a Quantum Design physical properties measurement system, i.e., Dynacool, which employs a standard thermal relaxation technique.

The x-ray diffraction patterns for representative concentrations are displayed in Fig. 1 with the data sets normalized to the highest peak intensity at 2θ = 36°.

![Fig. 1. (Color online) (a) Powder x-ray diffraction pattern for representative concentrations of LiIn(Cr$_{1-x}$Rh$_x$)$_2$O$_4$. The black, red, and blue data sets correspond to x = 0, 0.05, and 0.1 respectively. The measured intensity has been normalized to the highest peak at 2θ = 36° and the data sets have been offset for clarity. (b) The lattice parameter a versus the Rh concentration x. For all measured concentrations the lattice parameter increases linearly with x, starting from 8.338 Å for x = 0 up to 8.375 Å at x = 0.1 and is well described by $a = 8.3381(8) + 0.379(13)x$, represented by the black solid line.](image1.jpg)

Rietveld refinements were performed on the powder XRD patterns for each sample by using GSAS[17] and EXPGU1.[18] All of the x-ray diffraction data sets are consistent with a cubic $F43m$ crystal structure and the peak positions well fit with the theoretical peak positions. The lattice parameter, a, increases linearly with the Rh concentration and is displayed in Fig. 1(c). Furthermore, a follows the relation $a = 8.3381(8) + 0.379(13)x$ and is represented by the black solid line.

Illustrated in Fig. 2(a) is the magnetic susceptibility, $\chi$ versus $T$ for all measured Rh concentrations in an applied magnetic field of 1000 Oe, where $\chi$ is displayed as per Cr atom as Rh is expected to be non-magnetic.

![Fig. 2. (Color online) (a) Temperature dependence of $\chi$, for different concentrations of Rh from x = 0 up to x = 0.2 with an applied magnetic field of 1000 Oe. The Curie–Weiss fits were performed on temperatures above 100 K. The results of $\mu_{\text{eff}}$ and $\theta_{\text{CW}}$ are displayed in (b) and (c), respectively. Here $\mu_{\text{eff}}$ appears to be independent of $x$, staying near 3.85μB, represented by the black dashed line in panel (b), and $\theta_{\text{CW}}$ on the other hand shows a positive dependence with $x$, increasing linearly with $x$ for all the samples measured. The black dashed line in panel (c) is a guide to the eye.](image2.jpg)

For concentrations up to $x = 0.1$ there is a broad peak at roughly 50K that decreases in magnitude with increasing $x$, which becomes more broad and is slightly suppressed with increasing the Rh substitution. Above 100 K the magnetic susceptibility displays the Curie-Weiss behavior $\chi = C/(T - \theta_{\text{CW}})$. Displayed in Figs. 2(b) and 2(c) are the determined values for $\mu_{\text{eff}}$ ($\mu_{\text{eff}} \propto 2.83\sqrt{C}$) and $\theta_{\text{CW}}$, respectively. The value of $\mu_{\text{eff}}$/Cr stays constant near 3.85μB, close to Hund’s rule value of 3.87μB, and it is evident that there is no spin-orbit coupling in this system. Here $\theta_{\text{CW}}$ increases linearly with increasing Rh concentration, approaching lower negative values from -340 K for $x = 0$ up to -290 K for $x = 0.1$, showing that the system is becoming less antiferromagnetic with increasing Rh. At low temperatures $\chi$ appears to diverge, which has previously been attributed to orbital spins/magnetic impurities of 0.2%.[18]

Figure 3(a) displays the specific heat data as $C_p/T$ versus $T$ for concentrations of $x$ up to 0.2. The data is displayed per M atom ($M = \text{Cr or Rh}$) as both elements would contribute. For the $x=0$ sample a sharp peak is observed at $T_p = 14.3$ K (as shown by the black arrow in the graph). Initial Rh substitution rapidly suppresses $T_p$, but has a significantly diminished effect with further substitution as $T_p$ drops to 12.7 K for $x = 0.025$, and stays almost constant for higher $x$ as $T_p = 12.5$ K for $x = 0.1$. Interestingly the suppression of $T_p$ is noticeably slower than that observed in the LiGa$_{1-x}$In$_x$Cr$_2$O$_4$ system, which shows the complete suppression of $T_p$ at 6% Ga substitution.[19] It should be noted that previous investigations on LiInCr$_2$O$_4$ observed two features in the specific heat data: a sharp peak associated with a structural phase transition at $T_p = 15.9$ K and a shoulder at $T_S = 14$ K, which was associated with the antiferromagnetic transition. However, the same study also found that the doped sam-
samples only displayed the peak which became associated with the antiferromagnetic ordering, even in concentrations as small as 2.5%. Combined with the high sensitivity of $T_p$ to initial substitution (the 2.5% Ga substituted sample $T_p = 12.9$ while the $x = 0$ sample in this study displays $T_p = 14.3$K, much closer to $T_p = 15.9$K of the previously reported $x = 0$) suggests that the absence of a shoulder in the $x = 0$ sample is most likely due to the trace amounts of impurities. Additionally a small peak is observed at 4.2 K and 2.2 K for $x = 0.1$ and 0.2 respectively, which appears to be a separate feature from $T_p$ as it is still clearly observed for $x = 0.1$ at 12.5 K.

Displayed in Fig. 3(b) is the specific heat data plotted as $C_p/T$ versus $T^2$.

Fig. 3. (Color online) (a) Specific heat data displayed as $C_p/T$ versus $T$ for the samples with Rh concentrations up to $x = 0.2$. A pronounced peak is observed at 14 K for the $x = 0$ sample and systematically decreases in amplitude with increasing Rh up to $x = 0.1$ where the peak becomes a broad feature and by $x = 0.2$ no broad feature can be observed. (b) The specific heat data displayed as $C_p/T$ versus $T^2$ to highlight the linear behavior above $\sim 3000$K$^2$ (the $x = 0.2$ data set has been omitted for clarity). The inset displays $\gamma$ as a function of $x$ with the dashed red line serving as a guide to the eyes.

For all measured samples the data appear linear above roughly 3000 K$^2$ ($\sim 50$K) and are well described by $C = \gamma T + \beta T^3$, where the first and second terms correspond to the electronic and phonon contributions, respectively. This can be seen in Fig. 3(b) which displays the same data as Fig. 3(a) plotted as $C_p/T$ versus $T^2$, except for $x = 0.2$, which was omitted for clarity. The results for $\gamma$ are displayed in the inset of Fig. 3(b) and appears to decrease linearly with increasing Rh concentration, starting from $\sim 135$ mJ mol$^{-1}$K$^{-2}$ for low concentrations of Rh and decreasing down to 109 mJ mol$^{-1}$K$^{-2}$ for $x = 0.2$.

Displayed in Fig. 4 is $T_p$, the peak associated with the antiferromagnetic transition, versus chemical substitution for LiGa$_{1-y}$Cr$_{y}$O$_8$ taken from reported literature. In Fig. 5(a) and for LiIn(Cr$_{1-x}$Rh$_x$)$_2$O$_8$ in Fig. 3(b). Immediately it becomes clearer that the different chemical substitutions produce different responses in $T_p$. Rh substitution seems to have a slight effect on $T_p$, only decreasing from 14.3K for $x = 0$ down to 12.5 K for $x = 0.1$ while LiGa$_{1-y}$Cr$_{y}$O$_8$ displayed a more rapid suppression of $T_p$ where $y = 0.06$ completely suppressed $T_p$. The grey area in Fig. 4(b) represents the region of $x$, which is not investigated in this study and contains $x_{cr}$, i.e., the critical concentration where $T_p$ is fully suppressed.

![Fig. 4](image-url)
pyrochlores is unknown. However, the compressibility of the related spinel oxides is known and exhibits an almost universal value for $B_0$ (and therefore $kT$ as $kT = 1/B_0$) [22] including that of LiGaCr$_4$O$_8$ with $B_0 = 173$–210 GPa, [22] which was used as an estimate for the compressibility of the breathing pyrochlores. Comparing the chemical pressure from the critical concentrations of 10% Rh substitution and 6% Ga substitution appears to be comparable with the breathing factor $f$, and importantly the systems in which the frustration was introduced approaches $f = 0.07$ MPa for Rh substitution. For Ga substitution the change in lattice results in a positive chemical pressure with $P_{ch} = 0.05$–0.04 MPa for 6% Ga substitution. Recall that LiInCr$_4$O$_8$ is already near the limit of an isolated tetrahedral with $J'/J = 0.1$ (LiGaCr$_4$O$_8$ exhibits $J'/J = 0.6$), where $J'$ and $J$ are the nearest-neighbor magnetic interactions of the large and small tetrahedra formed by the Cr atoms. [12,15] Negative pressure from Rh substitution would reduce $J'$ while as $J'/J = 0.1$ and is already close to the limit of 0, additional negative pressure would have diminished effects such as a smaller change in $T_p$. On the other hand, the upper limit of $J'/J = 1$ is far off and therefore would not reduce the effects of positive chemical pressure from Ga substitution.

To better understand the relationship between the frustration and magnetic order in the breathing pyrochlores, it is important to characterize the amount of frustration. The previous investigation on LiGa$_y$In$_{1-y}$Cr$_4$O$_8$ characterized the frustration by the breathing factor $B_1 = J'/J$, with $B_1 = 0.6$ for LiGaCr$_4$O$_8$ and a much smaller $B_1 = 0.1$ for LiInCr$_4$O$_8$. [12,15] However, as this investigation directly alters the Cr occupying site with Rh substitution, it complicates the determination of $B_1$. Therefore in this study the frustration was instead characterized by the following equation $f = -\theta_{CW}/T^*$ [15], where $\theta_{CW}$ is determined from the Curie–Weiss fits to the magnetic susceptibility, and $T^*$ is the magnetic transition temperature, such as the Néel temperature for an antiferromagnet or spin-glass temperature. In this system, $T^*$ is the peak determined from the specific heat. From this analysis we find that $f = 22.6$ for $x = 0$ and slowly decreases with increasing Rh reaching 20.8 for $x = 0.1$ (there was no clear feature to determine $T_p$ for $x = 0.2$). Performing the same analysis of $f$ on LiGa$_y$In$_{1-y}$Cr$_4$O$_8$ we find that Ga substitution increases $f$ where $f = 35$ for $y = 0.05$ and approaches $f = 47$ for LiGaCr$_4$O$_8$ consistent with the increase in $B_1$ observed in the previous investigation of LiGa$_y$In$_{1-y}$Cr$_4$O$_8$. [12,15]

Both LiInCr$_4$O$_8$ and LiGaCr$_4$O$_8$ are engineered systems in which the frustration was introduced through the ‘breathing’ lattice, while importantly the amount of frustration appears to be comparable with the traditional frustrated materials. For example, the well known frustrated system ZnCr$_2$O$_4$ displays $f = 25$, similar to that of LiInCr$_4$O$_8$ and actually is less frustrated than LiGaCr$_4$O$_8$ with $f = 47$. [12,15] Using the singlet-triplet crossover temperature $T^* = 4K$, the other known breathing pyrochlore Ba$_3$Yb$_2$Zn$_2$O$_{11}$ displays $f = 32$ [15] comparable with the frustration in LiMT$_2$O$_8$. However, it should be noted that there are other materials with much larger $f$, such as the 2D spinel based Ba$_2$Sn$_2$Ga$_3$ZnCr$_2$O$_{22}$ which exhibits a much higher ratio of $f = 200$. [20]

In summary, we have performed a systematic investigation on the chemical substitution effects of the breathing pyrochlore LiIn(Cr$_{1-x}$Rh$_x$)$_4$O$_8$. From measurements of magnetic susceptibility and specific heat, we do not see any conclusive evidence of the non-Fermi liquid behavior. However, signatures of magnetic frustration are apparent, from magnetization a broad feature centered at roughly 40 K is slowly suppressed with increasing Rh, until $x = 0.1$ the feature is extremely broad and difficult to distinguish. From specific heat a peak at roughly 15 K for $x = 0$ is slightly suppressed with initial Rh substitution, staying at 14 K for $x$ up to 0.1 but by $x = 0.2$ the feature is completely suppressed. Furthermore, we find that the change in the electronic configuration or chemical pressure cannot fully explain the response of $T_p$. However, from these measurements we find that different chemical substitutions can be used to tune the amount of frustration which will be of great use for future attempts at uncovering new and enhanced magnetically frustrated systems.

References

[1] Gardner J S et al 2010 Rev. Mod. Phys. 82 53
[2] Bramwell S T and Gingras M J P 2001 Science 294 1495
[3] Raju N P et al 1992 Phys. Rev. B 46 5405
[4] Mandrus D et al 2001 Phys. Rev. B 63 155104
[5] Yang B J and Kim Y B 2010 Phys. Rev. B 82 064511
[6] Yonezawa S et al 2001 J. Phys. Soc. Jpn. 70 819
[7] Yonezawa et al 2001 J. Phys. Soc. Jpn. 70 1655
[8] Yonezawa et al 2001 J. Phys.: Condens. Matter 13 L9
[9] Gorter H R 1930 Nieuw Jb. Mineral. 61 1
[10] Greedan J E et al 1986 Solid State Commun. 59 895
[11] Sanders M B et al 2016 J. Mater. Chem. C 4 541
[12] Okamoto Y et al 2013 Phys. Rev. Lett. 110 097203
[13] Tanaka Y et al 2014 Phys. Rev. Lett. 113 227001
[14] Lee S et al 2016 Phys. Rev. B 93 174402
[15] Okamoto Y et al 2015 J. Phys. Soc. Jpn. 84 043707
[16] Martín-Belloso O, Moreo N O, Sanjurjo J A, Rittner C, García-Adesa A, H, Huber-Del, Osowski S, Batc, Chiggiato S W, Pagliuso P G, Sarsa J L and Martins G B 2001 J. Phys. Chem. B 89 7050
[17] Lammers A C and Vis Devreese B 2004 General Structure Analysis System Los Alamos National Laboratory Report LAUR p 86
[18] Tobu H 2001 J. Appl. Crystallogr. 34 210
[19] Kimura K et al 2014 Phys. Rev. B 90 060114(R)
[20] Hagemann I S et al 2001 Phys. Rev. Lett. 86 894
[21] Kanzian and N et al 2011 Phys. Rev. B 84 245122
[22] Recco J M et al 2001 Phys. Rev. B 63 184101
[23] Zhang L, Ji F G, Zhao F and Gong Z Z 2011 Chin. Phys. B 20 041702