Field-induced Bose-Einstein Condensation of triplons up to 8 K in Sr₃Cr₂O₈

A. A. Aczel,¹ Y. Kohama,² C. Marcenat,³ F. Weickert,⁴ M. Jaime,² O. E. Ayala-Valenzuela,² R. D. McDonald,² S. D. Selesnic,¹ H. A. Dabkowska,⁵ and G. M. Luke¹,⁵,⁶

¹Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada, L8S 4M1
²National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
³CEA-Grenoble, Institut Nanosciences et Cryogénie, SPSMS-LATEQS, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
⁴Max Planck Institute for Chemical Physics of Solids, Dresden, Germany
⁵Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada, L8S 4M1
⁶Canadian Institute of Advanced Research, Toronto, Ontario, Canada, M5G 1Z8

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Single crystals of the spin dimer system Sr₃Cr₂O₈ have been grown for the first time. Magnetization, heat capacity, and magnetocaloric effect data up to 65 T reveal magnetic order below applied fields of H₁ ~ 30.4 T and H₂ ~ 62 T. This field-induced order persists up to Tₓ max ~ 8 K at H ~ 44 T, the highest observed in any quantum magnet where H₂ is experimentally-accessible. We fit the temperature-field phase diagram boundary close to H₁ using the expression Tₓ = A(H-H₁)ν. The exponent ν = 0.65(2), obtained at temperatures much smaller than Tₓ max, is that of the 3D Bose-Einstein condensate (BEC) universality class. This finding strongly suggests that Sr₃Cr₂O₈ is a new realization of a triplon BEC where the universal regimes corresponding to both H₁ and H₂ are accessible at ⁴He temperatures.

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The Bose-Einstein condensate (BEC) is a unique state of matter in which a macroscopic number of bosons collapses into a global (identical) quantum state.⁴ Although superfluid ⁴He is possibly the most studied Bose-Einstein condensate (BEC) universal class. This finding strongly suggests that Sr₃Cr₂O₈ is a new realization of a triplon BEC where the universal regimes corresponding to both H₁ and H₂ are accessible at ⁴He temperatures.

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only one nearest neighbour (NN) magnetic ion they form spin dimers along the c-axis. While the $A^{2+}$ ions are essentially isolated from the $MO^{4-}$ tetrahedra, they seem to play an important role in controlling the NN M-M distance and the value of the associated spin gap. For example, while $Ba_3Cr_2O_8$ has a NN Cr-Cr distance of 3.9765 Å and a spin gap of 15.6(3) K \cite{10}, $Sr_3Cr_2O_8$ has a smaller NN Cr-Cr distance of 3.842 Å and hence a larger spin gap of 61.9(1) K \cite{11}. This is consistent with the expectation that a smaller NN distance between the magnetic ions should yield a larger antiferromagnetic intradimer exchange interaction. The stronger intradimer exchange interaction in the Sr-Cr system pushes the temperature scale of the magnetic order to the highest values observed yet in a system where $H_{\text{c2}}$ is experimentally-accessible.

Single crystals of $Sr_3Cr_2O_8$ were grown by the optical floating zone method at McMaster University. We first mixed together stoichiometric quantities of SrCO$_3$ and Cr$_2$O$_3$. The resulting powder was shaped into 10 - 12 cm long rods, which were annealed for 72 hours in air at 1200°C and then quenched to room temperature. The rods cracked during the annealing process, so they were remade following this and subsequently annealed for $\sim$5 hours in high purity Ar gas at 1200°C to strengthen them for the floating zone growths. Since $Sr_3Cr_2O_8$ is congruently melting in Ar gas, the crystals were grown at a very high rate of 20 mm/h with an Ar pressure of $\sim$170 kPa and a temperature of 1470°C. The phase purity of the resulting crystals was confirmed by powder x-ray diffraction, and they were aligned by Laue x-ray diffraction.

The anisotropy of the g-factor was measured via electron paramagnetic resonance (EPR) at 70 GHz using a resonant cavity mounted in a cryogenic goniometer, so as to rotate the sample and resonant environment in situ. The temperature was maintained at 30 K to ensure sufficient thermal population of the triplet state using a $^4$He flow cryostat. The magnetic field was applied using a superconducting solenoid and calibrated using the conventional EPR-marker DPPH. The g-factors were found to be $g_c = 1.938(6)$ and $g_{ab} = 1.950(1)$.

Fig. T depicts dc susceptibility measurements of our crystals. At high temperatures, the data follows a Curie-Weiss law. Below $\sim$ 40 K, the susceptibility decreases sharply with decreasing temperature, which is characteristic of non-magnetic spin-singlet ground state systems. The susceptibility measurements also reveal that this system is nearly isotropic. We fit the susceptibility data to an interacting dimer model of the form:

$$\chi_M = \frac{N_A(\mu_B g)^2}{k_B T (3 + \exp(J_0/T) + J'/T)} + \chi_0 + \frac{A}{T}$$  \hspace{1cm} (1)

where $N_A$ is Avogadro’s number, $\mu_B$ is the Bohr magneton, $J_0$ is the intradimer exchange constant, and $J'$ is the sum of the interdimer exchange constants. The last two terms represent contributions from Van Vleck paramagnetism/core diamagnetism and impurity/defect spins respectively. We fixed the g-factors in the fits to the values obtained by EPR. From the fitting, we found only $\sim$0.8% free $S = 1/2$ moments, and estimated the exchange constants to be $J = 61.5(3)$ K and $J' = 12(2)$ K. Note that the latter are actually best determined by inelastic neutron scattering \cite{12}.

Magnetization data was collected using an extraction magnetometer in conjunction with a $^3$He fridge and a 65 T short pulse (35 ms) magnet at the National High Magnetic Field Laboratory (NHMFL) in Los Alamos, New Mexico. The Fig. 1 inset shows $M(H)$ for the $H \perp \hat{c}$ orientation while sweeping the field up. $M(H)$ has a very small value up to $H_{\text{c1}} = 30.4$ T due to defects/impurities in the sample. Above $H_{\text{c1}} = 30.4$ T, the spin gap is closed resulting in a magnetically-ordered regime between $H_{\text{c1}}$ and $H_{\text{c2}} = 62$ T where $M(H)$ increases roughly linearly with $H$. Finally, above $H_{\text{c2}}$ $M(H)$ saturates as the system reaches the fully-polarized state.

To further characterize the field-induced order, heat capacity and MCE measurements were performed using a home-built calorimeter \cite{13, 21}. These measurements were conducted in a $^3$He fridge placed in the core of a 35 T resistive magnet at the NHMFL in Tallahassee, Florida. The MCE data was collected for the $H \perp \hat{c}$ orientation, sweeping the field both up and down at 3 T/min. The quasi-adiabatic MCE yields a sharp change in the sample temperature when entering or leaving a magnetically-ordered state to ensure entropy conservation \cite{22}.

Fig. 2(a) shows a color contour plot of the entropy as a function of temperature and field. $\Delta S$ was calculated from the MCE data using the equation:

$$\Delta S = \int \kappa(T - T_{\text{bath}}) \frac{dt}{T}$$  \hspace{1cm} (2)
FIG. 2: (color online) (a) Color contour plot of the entropy $S/T$ of Sr$_3$Cr$_2$O$_8$, as calculated from the MCE data. The phase boundary determined by MCE is shown with black dots. (b) Selected heat capacity data as obtained by the dual slope method. For 33 T, data was also collected by the standard relaxation method (black triangles).

where $\kappa$ is the thermal conductivity of the thermal link in the calorimeter, $T$ is the sample temperature, and $T_{bath}$ is the bath temperature. We measured $\kappa$ as a function of $T$ at both 0 and 33 T and found very little difference in the two curves, so the 33 T thermal conductivity data was used in all our calculations. The absolute entropy was then obtained by a calibration process using 31.5 T heat capacity data. We chose to plot $S/T$ to improve the contrast since the entropy associated with the transition drops quickly with decreasing temperature. As one crosses the phase boundary at a constant temperature, a peak in the entropy is clearly evident. This results because both the low-field gapped phase and the ordered phase above the transition should have small entropies. However, in the proximity of the transition we likely have fluctuations of the order parameter characteristic of a second order transition and hence a much higher entropy.

Heat capacity measurements are presented in Fig. 2(b) for the $H \parallel \hat{c}$ orientation. The majority of the data was collected using the dual slope method with a large delta $T$ [22]. The main advantage of this technique is that data can be collected quickly which is important for efficient use of power in high field resistive magnets. However, this often comes at a cost of reduced accuracy, and so data is generally collected for at least one applied field using the standard relaxation technique to compare the two methods directly. In the present case, this was done at 33 T (black triangles in Fig. 2(b)). The excellent agreement between the techniques suggests that the dual slope method estimates the heat capacity well in Sr$_3$Cr$_2$O$_8$.

The emergence of a lambda-like anomaly was clearly observed with an increasing applied field beyond $H_{c1} \sim 30.4$ T; this provides unambiguous evidence for the field-induced order in this system. The lambda anomaly is small for fields close to $H_{c1}$, but becomes much more prominent with increasing applied field as seen in Fig. 2(b). Heat capacity data was also collected for the $H \parallel \hat{c}$ orientation. Similar lambda anomalies were observed in that case, and the transition temperatures were systematically shifted down by only $\sim 0.2$ K for a given applied field. This indicates that Sr$_3$Cr$_2$O$_8$ is a very isotropic, as previously suggested by the susceptibility measurements.

The spin gap in Sr$_3$Cr$_2$O$_8$ is quite large, and so DC fields provided by resistive magnets can access only a very small region of the phase diagram. For this reason, we also performed MCE measurements in both the 50 T mid-pulse (300 ms) and 60 T long-pulse (2 s) magnets in Los Alamos. For these measurements, a tiny Sr$_3$Cr$_2$O$_8$ single crystal (200 x 100 x 50 $\mu$m$^3$) was inserted into a small, home-built calorimeter [24]. To the best of our knowledge, these were the first successful MCE experiments performed in a pulsed field facility.

Fig. 3 presents a phase diagram for the $H \parallel \hat{c}$ orientation of Sr$_3$Cr$_2$O$_8$ as obtained from our specific heat, MCE and M(H) experiments. The asymmetric nature of the dome is quite unusual for a triplon BEC system; further studies are required to understand this feature. From the heat capacity measurements, the ordering temperature for a given field was taken as the peak of the lambda-like feature. From the MCE data, the ordering temperature for a given field was determined by locating the extrema in the first derivative of the sample temperature with respect to field [12, 21]. Some selected upsweep MCE curves are superimposed on the phase diagram. For clarity reasons we show only one downsweep MCE curve; the sample temperature changes in the opposite manner to the upsweep data near the transition as expected. No irreversible/dissipative mechanisms typical for a first order phase transition were observed. Many MCE scans were completed at low temperatures so it would be possible to determine a critical exponent. The fitted data all must lie in the universal regime for the obtained critical exponent to be meaningful, and an earlier Monte Carlo simulation study [25] suggested that the universal regime extends no higher than $\sim 0.4T_{c1}^{\text{max}}$, where $T_{c1}^{\text{max}}$ is the maximum temperature of the magnetically-ordered regime. In the present case, we have determined that the top of the dome lies around 8 K. To ensure that we stayed within the universal regime, only the MCE data below 2.7 K was fit to a power law of the form: $T_c = A(H-H_{c1})^\nu$.

Although one can perform a three parameter fit, $H_{c1}$ and $\nu$ are not independent variables. For this reason, we resorted to a series of two parameter fits where $H_{c1}$ was
shows the result of fitting the data near H\textsubscript{c1} transitions, the MCE traces have been magnified. The inset shows the fitting data near H\textsubscript{c1} to a power law.

systematically fixed at different values and ν was determined from the fitting. Our best fit yielded ν = 0.65(2) with a corresponding H\textsubscript{c1} = 30.40(1) T. The former is in agreement with the expected value of 2/3 for a 3D BEC universality class, strongly suggesting that Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8} is a realization of a new triplon BEC.

Finally, let us comment here on the nature of the magnetically-ordered state in Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}. The spin structures in the ordered states of the isostructural systems Ba\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}[13] and Ba\textsubscript{3}Mn\textsubscript{2}O\textsubscript{8}[21] have both been determined previously, and the results were quite different. In the case of Ba\textsubscript{3}Mn\textsubscript{2}O\textsubscript{8}, a combination of single ion anisotropy and geometric frustration lead to both an incommensurate spiral spin phase and an Ising-type modulated structure in the ordered regime[21]. The shape and structure of the phase diagram for that material depends on the orientation of the system relative to the applied field. In sharp contrast, neutron measurements revealed a commensurate, collinear spin structure in Ba\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}[13]. This is likely a result of the geometric frustration being relieved due to a structural distortion courtesy of a co-operative Jahn-Teller effect[23]. A similar Jahn-Teller effect has been reported for Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}[27], suggesting that the spin structure of the ordered state is very similar to the case of Ba\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8}.

In summary, we have determined the full (H,T) phase diagram for Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8} from both thermodynamic measurements and high-field magnetization. This phase diagram provides direct evidence for field-induced order in this system between H\textsubscript{c1} ~ 30.4 T and H\textsubscript{c2} ~ 62 T, with an unprecedented maximum ordering temperature T\textsubscript{cmax} ~ 8 K. The phase boundary near H\textsubscript{c1} was fit to a power law. Our obtained critical exponent of 0.65(2) agrees with the 3D BEC universality class, and so this strongly suggests that Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8} is a realization of a new triplon BEC system. Since a large portion of the universal regime in this material can be accessed via \textsuperscript{3}He systems, both the H\textsubscript{c1} and H\textsubscript{c2} quantum critical regimes can be studied in detail. This may help us to understand the asymmetric nature of the phase diagram and other more general aspects of triplon BEC phenomena. Note that no experimental criticality studies near H\textsubscript{c2} have been reported for triplon BEC systems to-date.

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FIG. 3: (color online) Sr\textsubscript{3}Cr\textsubscript{2}O\textsubscript{8} phase diagram with selected MCE traces superimposed and the ordered region shaded as a guide to the eye. Due to small temperature changes at the transitions, the MCE traces have been magnified. The inset shows the result of fitting the data near H\textsubscript{c1} to a power law.

[1] E.A. Cornell and C.E. Wieman, Rev. Mod. Phys. 74, 875 (2002).
[2] W. Ketterle, Rev. Mod. Phys. 74, 1131 (2002).
[3] A.F.G. Wyatt, Nature 391, 56 (1998).
[4] L.P. Pitaevskii and S. Stringari, Bose-Einstein Condensation, Clarendon Press, Oxford (2003).
[5] S.O. Demokritov et al., Nature 443, 430 (2006).
[6] T. Giamarchi and A.M. Tsvelik, Phys. Rev. B 59, 11398 (1999).
[7] T. Matsumbara and H. Masuda, Prog. Theo. Phys. 16, 569 (1956).
[8] A. Oosawa et al., J. Phys. Cond. Matt. 11, 265 (1999).
[9] T. Nikuni, M. Oshikawa, A. Oosawa, and H. Tanaka, Phys. Rev. Lett. 84, 5686 (2000).
[10] M. Jaime et al., Phys. Rev. Lett. 93, 087203 (2004).
[11] V.S. Zapf et al., Phys. Rev. Lett. 96, 077204 (2006).
[12] A.A. Aczel et al., Phys. Rev. B. 79, 100409(R) (2009).
[13] M. Kofu et al., Phys. Rev. Lett. 102, 177204 (2009).
[14] S.E. Sebastian et al., Nature 441, 617 (2006).
[15] For a recent review, see: T. Giamarchi, C. Ruegg, and O. Tchernyshyov, Nature Physics 4, 198 (2008).
[16] T. Nakajima, H. Mitamura, and Y. Ueda, J. Phys. Soc. Jpn. 75, 054706 (2006).
[17] M. Uchida, H. Tanaka, M.I. Bartashevich, and T. Goto, J. Phys. Soc. Japan 70, 1790 (2001).
[18] Y. Singh and D.C. Johnston, Phys. Rev. B 76, 012407 (2007).
[19] A.A. Aczel, H.A. Dabkowski, P.R. Provencher, and G.M. Luke, J. Cry. Growth 310, 870 (2008).
[20] D. Quintero-Castro et al., arXiv:0909.3911 (unpublished).
[21] E.C. Samulon et al., Phys. Rev. B 77, 214441 (2008).
[22] A.V. Silhanek et al., Phys. Rev. Lett. 96, 137203 (2006).
[23] S. Riegel and G. Weber, J. Phys. E: Sci. Instrum. 19, 790 (1986).
[24] Y. Kohama, C. Marcenat, and M. Jaime, in preparation
[25] N. Kawashima, J. Phys. Soc. Japan 73, 3219 (2004).
[26] M. Kofu et al., Phys. Rev. Lett. 102, 037206 (2009).
[27] L.C. Chapon, C. Stock, P.G. Radaelli, and C. Martin, arXiv:0807.0877 (unpublished).