$^7$Li NMR, magnetic susceptibility, and heat capacity studies on the triangular lattice system LiCrO$_2$.

L. K. Alexander,$^1$ N. Büttgen,$^2$ R. Nath,$^2$ A. V. Mahajan,$^1$ and A. Loidl$^2$

$^1$Department of Physics, Indian Institute of Technology, Mumbai 400076, India
$^2$Experimentalphysik V, Elektronische Korrelationen und Magnetismus, Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany.

(Date textdate; Received textdate; Revised textdate; Accepted textdate; Published textdate)

Abstract

We report $^7$Li NMR, magnetic susceptibility, and heat capacity measurements on the triangular lattice Heisenberg antiferromagnet compound LiCrO$_2$. We find that in contrast to NaCrO$_2$, magnetic properties of LiCrO$_2$ have a more pronounced three dimensional character with sharp anomalies in the temperature variation of the $^7$Li NMR intensity and the NMR spin-lattice relaxation rate $1/T_1$. From heat capacity measurements we find that the total entropy related to the magnetic transition is in agreement with expectations. However, we find a significant contribution to the magnetic entropy in the range from the ordering temperature $T_N$ to nearly $4T_N$. This suggests the existence of magnetic correlations at temperatures well above $T_N$ which might be due to the frustrated nature of the system. Based on the temperature dependence of $1/T_1$, we discuss the possible occurrence of a Kosterlitz-Thouless-Berezinskii transition taking place at $T_{KTB} = 55$ K in LiCrO$_2$. Lithium depletion has no significant effect on the magnetic properties and the behaviour of Li$_{0.5}$CrO$_2$ is nearly unchanged from that of LiCrO$_2$. 

1
I. INTRODUCTION

Geometrically frustrated systems are being widely studied due to the possibility of unconventional ground states and their susceptibility to weak perturbations. The two-dimensional triangular lattice Heisenberg antiferromagnet (TLHAF) is a prominent example where exotic magnetic phenomena have been observed. Specifically, while Na$_x$CoO$_2$.1.3H$_2$O is superconducting (0.25 < x < 0.33), the unhydrated Na$_x$CoO$_2$ also shows a gamut of magnetic transitions$^{1,2,3}$. Presumably with the above background, Olariu et al.$^4$ investigated NaCrO$_2$ by nuclear magnetic resonance (NMR) and muon spin resonance ($\mu$SR) experiments (in addition to bulk probes) and thereby concluded to have observed for the first time an ”extended fluctuating regime” in TLHAF. Recent reports on NiGa$_2$S$_4$ (ref. 5) suggest an unconventional magnetic ground state originating from magnetic correlations which extend beyond nearest neighbours.

In this paper we present a detailed study of the magnetism and heat capacity of LiCrO$_2$ using both macroscopic and local probes. Further, in view of the important role played by sodium ions in Na$_x$CoO$_2$, measurements on the delithiated compound Li$_{0.5}$CrO$_2$ are also presented. Previous work on LiCrO$_2$ has established that it possess $\alpha$–NaFeO$_2$ type structure comprising two-dimensional triangular chromium layers$^6$. Magnetic susceptibility data$^6,7$ indicate a transition at around 62 K. Published susceptibility data could be fitted with a Curie-Weiss law only above 450 K and the paramagnetic Curie temperature is reported in the range 570 K to 700 K$^6,7,8$. Neutron scattering and Raman scattering studies$^9,10,11$ suggest a 3D character to the magnetic correlations below the transition temperature ($T_N$). Above $T_N$, measurements indicate a wide region showing short-range magnetic correlations$^8$. There are no NMR studies or specific heat measurements reported on the compound till date.

Herein, we report bulk susceptibility, $^7$Li NMR studies, and specific heat measurements carried out on Li$_x$CrO$_2$. ($x = 1, 0.5$). We found that the $^7$Li NMR spectral intensity of the title compounds drops precipitously at $T_N$ unlike in NaCrO$_2$ where the intensity drops progressively in a 10 K range below $T_N$. The ”extended fluctuating regime” observed in NaCrO$_2$ does not appear pronounced in LiCrO$_2$. Our heat capacity measurements exhibit a peak at the magnetic ordering temperature. Both NMR and specific heat studies suggest that magnetic correlations develop well above $T_N$. The rest of the paper is organised as follows. Section II contains the experimental details, wherein synthesis and structural characteris-
tion of Li$_2$CrO$_2$, experimental set-up and parameters for various other measurements such as bulk magnetic susceptibility, specific heat, and NMR are included. In section III, we present the results of our measurements which is followed by a comprehensive discussion in section IV.

II. EXPERIMENTAL DETAILS

Polycrystalline LiCrO$_2$ was synthesised by solid-state reaction of a stoichiometric mixture of Li$_2$CO$_3$ (Aldrich, 99.99 %) and Cr$_2$O$_3$ (Aldrich, 98.0%). The mixture was fired at 800°C for 48 hours with one intermediate grinding. X-ray diffraction experiment was carried out using PANalytical X’pert PRO powder diffractometer with X’celerator detector. The diffractometer uses a Cu-K$_\alpha$ target ($\lambda_{av} = 1.54182$ Å). Our results (see Fig. 1(a)) indicate single phase formation and the peaks can be indexed using the trigonal space group, $R\bar{3}m$. Using a least-squares method, the lattice parameters were found to be $a = 2.8949(12)$ Å, $b = 2.8949(12)$ Å, and $c = 14.3886(98)$ Å. As shown in a sketch of the LiCrO$_2$ crystal structure (Fig. 2), Cr layers have a triangular configuration. In the structure, oxygen ions form ABCABC type of stacking layers. Also, the edge shared Cr octahedral layers are separated by Li ions. The crystal structure makes a strong case for 2D triangular lattice Heisenberg antiferromagnets.

Li$_{0.5}$CrO$_2$ was prepared by extraction of lithium from LiCrO$_2$ using chemical methods. The extraction was carried out by stirring LiCrO$_2$ powders in an aqueous solution of an oxidising agent, Na$_2$S$_2$O$_8$ (Thomas Baker, 99.0 %) for two days with help of a magnetic stirrer. The amount of Na$_2$S$_2$O$_8$ required for the delithiation reaction was decided based on our experience with LiCoO$_2$. The delithiation reaction for synthesis of Li$_{0.5}$CrO$_2$ can be summed up as:

$$2\text{LiCrO}_2 + 0.5 \text{Na}_2\text{S}_2\text{O}_8 \rightarrow 2 \text{Li}_{0.5}\text{CrO}_2 + 0.5 \text{Na}_2\text{SO}_4 + 0.5 \text{Li}_2\text{SO}_4$$

The product was filtered, washed repeatedly - first with water and finally with acetone, and air-dried. In order to estimate the level of delithiation in LiCrO$_2$, $^7$Li NMR spectral intensities were compared. Here, the NMR spectra were measured in the un-delithiated and the delithiated samples under identical conditions and normalised by the respective sample masses. Based on this, Li$_{0.5}$CrO$_2$ should be written as Li$_{(0.51 \pm 0.02)}$CrO$_2$. XRD pattern of Li$_{0.5}$CrO$_2$ was found to match exactly with that of LiCrO$_2$ (Fig.1(b)). Lattice parameters
of Li$_{0.5}$CrO$_2$ do not vary significantly from those of LiCrO$_2$ quoted in the above paragraph.

Macroscopic magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer (MPMS5, Quantum Design) and a vibrating sample magnetometer (VSM) from Quantum Design. Magnetization ($M$) was measured as a function of temperature ($T$) in an applied field ($H$) of 1 T, in a temperature range 2 K-300 K. The $M$-$H$ isotherms were measured at 280 K, 200 K, 150 K, and 50 K. None of these $M$-$H$ plots (not shown) exhibited any signs of hysteresis. Ferromagnetic impurities estimated using the plots were found to be negligible. Zero-field cooled (ZFC) and field cooled (FC) magnetization measurements were carried out on both the samples. In this experiment, sample was first cooled in zero applied field to 2 K and then the measurements were taken from 2 K to 300 K in a field of 50 G (ZFC data). Whereas for the FC measurements, sample was cooled in an applied field of 50 G. Then in the same field, data were collected in the temperature 2 K to 300 K.

Solid-state NMR is an efficient local probe of magnetic properties. This technique allows one to study static magnetic correlations and low-energy spin excitations. Our NMR experiments were carried out using a home-built NMR spectrometer. We used an Oxford Instruments (sweepable) superconducting magnet and a variable temperature insert. In the experiments, $^7$Li nuclei (nuclear spin $I =3/2$ and gyromagnetic ratio $\gamma/2\pi = 16.546$ MHz/Tesla) were probed using pulsed NMR technique. Measurements were carried out in the temperature range, 2 K - 300 K. Spectra were obtained employing Fourier transform (FFT) technique at a fixed field of 1.089 T. At low temperatures (below 10 K), since the spectra were too broad for an accurate FFT experiment, field sweep measurement at a frequency of 18 MHz were carried out to supplement the spectral data. In order to check the field dependence for the NMR characteristics of the compound, measurement were also done at a higher applied field; by sweeping the field at 71 MHz (applied field $H \approx 4.3$ T). It also allows to investigate the field dependence of the extended fluctuation regime, if any. An aqueous solution of LiCl was used as the diamagnetic reference. NMR spin echoes were obtained using $\pi/2 - \tau - \pi$ pulse sequences. NMR experiments at two different frequencies were performed in order to check if there is any field dependence for the NMR characteristics of the compounds. At 18 MHz, $\pi/2$ pulse widths were typically in the range $1 - 8 \mu$s for LiCrO$_2$ and Li$_{0.5}$CrO$_2$. At 71 MHz, typical $\pi/2$ pulse widths were $4 \mu$s. For spin-lattice relaxation measurements, inversion recovery method was employed. The spin-spin relaxation
rate \((1/T_2)\) was determined by measuring the decay of echo intensity as a function of the separation between the \(\pi/2\) and \(\pi\) pulse.

Specific heat measurements were carried out on LiCrO\(_2\) in the temperature range 3 K to 300 K using a Quantum Design PPMS system. LiCoO\(_2\) is a non-magnetic equivalent\(^{13}\) of LiCrO\(_2\) having the same crystal structure. Therefore, in order to extract the magnetic part of specific heat of LiCrO\(_2\), isostructural LiCoO\(_2\) was measured. For this purpose, LiCoO\(_2\) was prepared as reported elsewhere\(^{13}\).

### III. RESULTS

**A. Bulk magnetic susceptibility**

The temperature dependence of bulk magnetic susceptibility \(\chi(T) = M/H\) for both LiCrO\(_2\) and Li\(_{0.5}\)CrO\(_2\) are shown in figure 3. In both the samples, one can see that \(\chi\) increases with decreasing temperature till a broad maximum is reached at about 65 K and below this temperature \(\chi\) is nearly constant. In line with the reported results\(^{6,7,8}\), we found that the susceptibility data of LiCrO\(_2\) do not obey the Curie-Weiss law below 300 K. A negligible low-temperature Curie tail implies the presence of very low amounts of paramagnetic impurities and the high quality of our samples. The 65 K anomaly in LiCrO\(_2\) has been associated with antiferromagnetic (AF) order\(^{9,10}\). A nearly constant (but somewhat higher) value of susceptibility for Li\(_{0.5}\)CrO\(_2\) compared to LiCrO\(_2\) through the entire temperature region measured and a slightly enhanced low-temperature Curie-tail appears to indicate that delithiation has generated small amounts of paramagnetic impurities which remained even after repeated washing. Figure 4 shows ZFC and FC magnetisation data for LiCrO\(_2\). There, one observes a splitting of the ZFC and FC curves at around 240 K. This history dependent magnetization for LiCrO\(_2\) has not been reported till now. In the case of Li\(_{0.5}\)CrO\(_2\), as well, we observed roughly the same features as that of LiCrO\(_2\). We checked for the possible origin of this ZFC-FC splitting from any unnoticed impurities (in spite of the negligible Curie tail, and the single phase x-ray diffraction spectrum), especially oxides of chromium. CrO\(_2\) has a ferromagnetic transition temperature of 400 K. Cr\(_2\)O\(_3\) and Cr\(_2\)O\(_5\) have antiferromagnetic transitions at 307 K and 125 K, respectively. This practically rules out impurities as a cause for the 240 K anomaly. An intrinsic reason for the history
dependent magnetisation observed in Li$_x$CrO$_2$ is then indicated.

B. NMR measurements

1. Spectra

As seen in Fig. 2, the Li nuclei can have a hyperfine coupling (presumably via the oxygen ions) with the magnetic Cr$^{3+}$ ions which are present in triangular planes above and below the Li planes. The spin susceptibility of the Cr$^{3+}$ ions $\chi_{\text{spin}}(T)$ gives rise to a shift of the $^7$Li resonance $K(T)$ following Eq. (1):

$$N_A \mu_B K(T) = A_{hf} \chi_{\text{spin}}(T)$$

where $N_A$ is the Avogadro number, $\mu_B$ is the Bohr magneton, and $A_{hf}$ is the hyperfine coupling constant. In both LiCrO$_2$ and Li$_{0.5}$CrO$_2$ at both the frequencies, 18 MHz and 71 MHz, we found that the spectra have a small temperature dependence for the shift. This nature of variation is expected since the absolute variation of the susceptibility from 300 K to 60 K is itself very small. Figure 5 shows variation of NMR shift with temperature for LiCrO$_2$ above the region of the transition temperature. The inset shows a plot of $K$ versus bulk susceptibility $\chi$ with temperature as an implicit parameter. From this plot, using Eq. (1), the hyperfine coupling constant $A_{hf}$ was estimated to be $6 \pm 1$ kG /$\mu_B$. This result suggests a weak hyperfine coupling between Li and Cr. This is in agreement with the results on NaCrO$_2$ (ref. 4).

Figure 6 shows the spectra of LiCrO$_2$ in the region of transition. Integrated spectral intensity, which is proportional to the number of $^7$Li nuclei, is roughly constant above 70 K. At around 62 K, intensity falls sharply - as also shown in figure 7 (corrected for temperature and $T_2$ effects). This sharp decline indicates the onset of long-range order. The signal disappears completely at around 55 K. In a conventional case, the spectra broaden as one approaches the ordering temperature from above and eventually disappear (from the window of observation) below the ordering temperature due to the large static field that develops in the ordered state. Here in LiCrO$_2$ at 1 T, the $^7$Li NMR signal reappeared at around 35 K. By around 12 K, a small signal could be observed but the spectrum was too broad to reliable obtain the lineshape using FT techniques. Therefore, in figure 7, data shown
below 10 K were taken by sweeping the field at 18 MHz. Resultant spectra are shown in the inset of figure 6. Here in LiCrO$_2$, unlike the case of NaCrO$_2$ (ref. 4), intensity is not regained completely down to 4 K. Spectra of Li$_{0.5}$CrO$_2$ also showed a similar temperature dependence.

Spectra of LiCrO$_2$ in 4.3 T showed a qualitatively similar behaviour with small differences. The intensity sharply falls at around 63 K and continues to fall till about 52 K. The signal is never completely lost and about 30% of the signal is regained by about 8 K.

2. Spin-lattice relaxation rate $1/T_1$

In LiCrO$_2$ and Li$_{0.5}$CrO$_2$, for $H \approx 4.3$ T and 1 T, the recovery of the nuclear magnetisation after an inverting pulse was single exponential. The recovery data fitted well to the expression,

$$\left(\frac{M(t)-M_\infty}{2M_\infty}\right) = Ae^{(-t/T_1)} + C$$

where $M(t)$ is the nuclear magnetisation at a time $t$ after an inverting pulse and $M_\infty$ is the equilibrium value of the magnetisation. Temperature dependence of $1/T_1$ for $H \approx 1$ T for LiCrO$_2$ is presented in figure 8. In LiCrO$_2$, the spin-lattice relaxation rate shows a divergence around 63 K due to slowing down of fluctuations as one approaches magnetic order. This is around the same temperature at which a broad maximum in the bulk susceptibility $\chi(T)$ was observed, accompanied by an intensity loss of the NMR spectra. Below 59 K, the $^7$Li signal was very weak and broad and did not allow for complete saturation for accurate relaxation rate measurements.

At 71 MHz ($H \approx 4.3$ T), relaxation rates were measured between 250 K to 80 K. The results were in reasonable agreement with those at 18 MHz. Measurements on Li$_{0.5}$CrO$_2$ at 18 MHz gave results similar to those on LiCrO$_2$.

C. Specific heat capacity

Results of the specific heat measurements are shown in figure 9. Inset shows the temperature dependence of specific heat capacity of LiCrO$_2$ and LiCoO$_2$. Layered LiCoO$_2$ is non-magnetic and isostructural with LiCrO$_2$. Also, in a Debye model picture, the Debye temperatures of the two compounds are expected to be nearly the same taking into account
their molecular weights and unit cell volumes. Indeed, at high temperatures, the heat capacities of the two compounds coincide. The magnetic contribution to the specific heat of LiCrO$_2$ ($C_{\text{mag}}$) was determined by subtracting the specific heat of LiCoO$_2$ from that of LiCrO$_2$. $C_{\text{mag}}$ shows a peak at around 63 K, in good agreement with anomalies observed by us in bulk magnetic susceptibility and NMR measurements.

IV. DISCUSSION

The magnetic susceptibility of LiCrO$_2$ has been reported by several groups. The main conclusion has been that a Curie-Weiss behaviour (indicative of non-interacting local moments) is valid only above about 400 K. A large range from 400 K to 63 K (at which long-range order finally sets in) in which magnetic correlations are present is probably due to the frustrating magnetic interactions of the triangular Cr planes.

We found that delithiation of LiCrO$_2$ did not have a significant impact on its magnetic properties. This is quite unlike the case of NaCoO$_2$ where the magnetic ground state depends strongly on the Na content. This implies that the smaller Li ion does not impact the magnetism of the Cr layers nor does it contribute mobile charge carriers in the planes.

As seen from the structure, each Li has a super-transferred hyperfine coupling to the Cr layers via oxygen ions. Since seven Cr ions (three ions from three triangles of which two ions are common) from each layer might be expected to affect each Li, the Li senses a distribution of susceptibilities and hence a linewidth which increases with decreasing temperature as also with increasing field. In the ordered state, a 120° alignment of the spins on the vertices of the triangles will give a cancellation of hyperfine fields at the Li site. The linewidth might remain large due to any structural and magnetic disorder. In the case of NaCrO$_2$, an extended fluctuating regime was reported below $T_N$ and the full NMR signal intensity was recovered by about 10 K. While Olariu et al. did not show NMR $1/T_1$ data for NaCrO$_2$, their relaxation rate data from $\mu$SR showed a peak at 30 K which is much lower than the ordering temperature of 40 K in that compound. They therefore concluded that an extended fluctuating regime exists for NaCrO$_2$ below its $T_N$. On the other hand, our $^7Li$ NMR spin-lattice relaxation rate for LiCrO$_2$ diverges at $T_N$. Also, preliminary $\mu$SR measurements on our samples of LiCrO$_2$ have indicated the absence of an extended fluctuation regime below $T_N$. A stronger interplane interaction in LiCrO$_2$ as compared to NaCrO$_2$ is also indicated.
Theoretical study by Kawamura et al.\textsuperscript{16} have suggested the occurrence of Kosterlitz-Thouless-Berezinskii type of phase transition\textsuperscript{17,18,19} in 2D triangular lattice antiferromagnets, complimented by the inherent frustration effects. Here, the correlation between the spins generate vortices which stay as bounded pairs at low temperatures. But at a critical temperature, $T_{KTB} \neq 0$, these bounded vortex-antivortex pairs dissociate to free vortices resulting in a topological phase transition. Spin-lattice relaxation measurements can provide clues for the order driven by the free vortices at temperatures above $T_{KTB}$ in 2D antiferromagnets\textsuperscript{20,21}. For $T > T_{KTB}$, spin-lattice relaxation rate $1/T_1$ has two contributions: The first due to free vortices and the second due to spin-wave excitations, as given in the equation below.

$$\frac{1}{T_1} = \frac{(\gamma A_{hf}/2\pi)^2}{\sqrt{\pi n_v U}} + \alpha T + \beta$$ \hspace{1cm} (2)

where $A_{hf}$ is the hyperfine coupling constant, $\gamma$ is the gyromagnetic ratio for $^7$Li, and corresponding to a 2D correlation length of $\xi$, $n_v = 1/(2\xi)^2$ is the density of free vortices\textsuperscript{22}:

$$n_v = \left(\frac{1}{2\xi_0}\right)^2 \exp\left(\frac{-2b}{\sqrt{\tau}}\right)$$ \hspace{1cm} (3)

where, $\tau = (T/T_{KTB}) - 1$ and $\xi_0 \simeq a$, the lattice parameter and $b$ is a scaling parameter. The ideal value for $b$ is $\pi/2$, but theoretical calculation and later experimental reports\textsuperscript{20,21,23} allow for smaller values. Free vortices move through the lattice inducing spin flipping and the vortex velocity $U$ (ref. 24) is given by

$$U = \left[\frac{\pi}{2} \left(\frac{JS^2a^2}{h}\right)^2 n_v \ln \frac{k_B T_{KTB}}{JS^2n_v a^2}\right]^{1/2}$$ \hspace{1cm} (4)

The solid-line in figure 8 shows fit of Eq. (2) to our $1/T_1(T)$ data, assuming $A_{hf} = 6$ kG / $\mu_B$ (from the $K$ vs $\chi$ plot- Fig. 5), $b = 0.86$ and $J/k_B = 40$ K (from the report by Delmas et al.\textsuperscript{2}). The corresponding $T_{KTB}$ for LiCrO$_2$ was found to be 55 K which is close to the value obtained by Ajiro et al.\textsuperscript{25} of 60 K and might explain the temperature dependence of the spin-lattice relaxation rate above $T_N$.

The coefficient of the linear term in Eq. (2) was found to be, $\alpha = 0.45$ sec$^{-1}$K$^{-1}$. As mentioned earlier, the linear increase in $1/T_1$ data at temperatures above 120 K can be attributed to spin-wave excitations. But in the paramagnetic ( high temperature) limit, one expects the relaxation rate value to level off - as the fluctuations of local moments is
fast and random. In a case where the nuclear relaxation mechanism is mainly governed by fluctuations of localised spins, $1/T_1(T)$ in the high temperature limit, $1/T_1\propto$ is given by

$$\frac{1}{T_1\propto} = \sqrt{\frac{2\pi}{\gamma g \mu_B A_{hf}}} \left( \frac{z'}{z} \right)^2 \frac{S(S+1)}{3\omega_{ex}}$$

(5)

where $\omega_{ex}$ is the exchange frequency of local moments given by $\omega_{ex} = \frac{k_B |\theta_{CW}|}{\hbar \sqrt{z S(S+1)/6}}$. $z$ and $z'$ are the number of local moments exchange coupled with each other (= 6, here) and that of local moments interacting with the probing nuclei (= 6, here) at non-magnetic crystal sites, respectively. The other parameters represent usual physical constants. For LiCrO$_2$, $g = 1.98$, was taken from reports of EPR measurements by Moreno et al. Thus, using Eq. (5), spin-lattice relaxation rate of LiCrO$_2$ in the paramagnetic region was found to be 190 sec$^{-1}$. The linear increase in $1/T_1$, with temperature, observed by us above 120 K will yield a value of 190 sec$^{-1}$ at about 470 K; i.e. LiCrO$_2$ seems to reach the paramagnetic limit only at 470 K. This finding is in agreement with $\chi(T)$ data which found $|\theta_{CW}| \sim 570 - 700$ K.

The heat capacity of non-magnetic LiCoO$_2$ could be fit reasonably well in the full temperature range using the Debye model which yields for the specific heat at constant volume $C_v$

$$C_v = 9r N_A k_B \left[ \frac{4T^3}{\theta^3} \right] \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} - \frac{\theta/T}{e^{\theta/T} - 1}$$

(6)

where $r$ is the number of atoms per formula unit, $N_A$ is the Avogadro’s number and $k_B$ is the Boltzmann constant, and $\theta$ is the Debye temperature. For LiCoO$_2$, $\theta$ was found to be about 800 K.

The total entropy related to magnetic order in LiCrO$_2$ can be determined by finding the area under the curve of the $C_{mag}/T$ vs $T$ plot of figure 9. We obtained a value of 11.65 J/mol-K for the magnetic entropy $S_{mag}$ which is in reasonable agreement with the expected value $R \ln(2S + 1) = 11.53$ J/mol-K where $R$ is the gas constant and $S = 3/2$ for Cr$^{3+}$. Nearly 80% of the contribution to the magnetic entropy change for LiCrO$_2$ comes from temperatures above $T_N$. This appears similar to the case of NaCrO$_2$ but in contrast to the entropy behaviour in conventional long-range ordered materials.

Below 240 K, Li$_x$CrO$_2$ shows a small history dependence (difference between the ZFC and FC susceptibility curves). This ZFC-FC splitting might be connected to the formation of
frozen magnetic clusters, which are singular regions with quite local magnetic interactions. Such a history dependence at temperatures much above the transition temperature has been reported earlier in geometrically frustrated compounds like Li$_{x}$Zn$_{1-x}$V$_{2}$O$_{4}$ (0 $\leq$ $x$ $\leq$ 0.9) [ref. 28,29] and Tb$_{2}$Mo$_{2}$O$_{7}$ [ref. 30]. Here in LiCrO$_{2}$, the origin of the clusters may be from the complex intra-layer magnetic correlations additionally influenced by the possible presence of free vortices.

The measurements show that LiCrO$_{2}$ is long range ordered below 62 K. The bulk magnetic susceptibility and magnetic specific heat, $C_{mag}$ suggests the presence of a short-range order in LiCrO$_{2}$ even at temperatures well above 62 K. Susceptibility data show a relatively weak anomaly at the ordering temperature. NMR spin-lattice relaxation data suggests the presence of free vortices in the lattice above 62 K. From our $^{7}$Li NMR relaxation rate analysis, based on expectations for a pure Kosterlitz-Thouless-Berezinskii system, we determined $T_{KTB}$ = 55 K. In the present system, however, inter-plane interactions lead to long-range order below 62 K.

V. CONCLUSION

In summary, we have performed $^{7}$Li NMR, bulk susceptibility, and heat capacity measurements on the TLHAF LiCrO$_{2}$. Anomalies in the NMR intensity, spin-lattice relaxation rate, bulk susceptibility, and heat capacity indicate an antiferromagnetic ordering temperature ($T_{N}$) of about 62 K in LiCrO$_{2}$. An extended fluctuating regime below $T_{N}$ appears to be much less prominent in LiCrO$_{2}$ compared to NaCrO$_{2}$. The interplanar magnetic interactions, as well, are therefore stronger in LiCrO$_{2}$ compared to NaCrO$_{2}$. A significant magnetic contribution to the specific heat exists above $T_{N}$. Magnetic susceptibility and specific heat data suggest presence of considerable amount of magnetic short-range order even at temperatures well above $T_{N}$. This is corroborated by the temperature dependence of the $^{7}$Li nuclear spin-lattice relaxation rate $1/T_{1}(T)$ above $T_{N}$ which was modeled to arise from free moving vortices in the LiCrO$_{2}$ lattice. Our value of $T_{KTB}$ = 55 K is similar to that estimated by Ajiro et al.$^{25}$ of 60 K. Li depletion does not have a significant effect on the magnetic properties of LiCrO$_{2}$ in contrast to isostructural NaCoO$_{2}$. More experiments and theoretical investigations on TLHAF’s are needed to obtain a full understanding of their
static and dynamic magnetic properties.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft via the Sonderforschungsbereich 484 (Augsburg) and partly by BMBF via VDI/EK M, FKZ 13N6917. We acknowledge helpful discussions with P. Mendels.

1. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian and T. Sasaki, Nature (London) 422, 53 (2003).
2. J. Sugiyama, J. H. Brewer, J. Ansaldo, H. Itahara, T. Tani, M. Mikami, Y. Mori, T. Sasaki, S. Hébert, and A. Maignan, Phys. Rev. Lett. 92, 017602 (2004).
3. M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, Phys. Rev. Lett. 92, 247001 (2004).
4. A. Olariu, P. Mendels, F. Bert, B. G. Ueland, P. Schiffer, R. F. Berger, and R. J. Cava, Phys. Rev. Lett. 97, 167203 (2006).
5. S. Nakatsuji, Y. Nambu, H. Tonomura, O. Sakai, S. Jonas, C. Broholm, H. Tsunetsugu, Y. Qiu, Y. Maeno, Science 309, 1697 (2005).
6. A. Tauber, W. M. Moller, and E. Banks, J. Sol. State Chem. 4, 138 (1972).
7. C. Delmas, G. Le Flem, C. Fouassier and P. Hagenmuller, J. Phys. Chem. Solids 39, 55 (1978).
8. N.O. Moreno, C. Israel, P.G. Pagliuso, A.J. Garcia-Adeva, C. Rettori, J.L. Sarraoa, J.D. Thompson, and S.B. Oseroff, J. Magn. Magn. Mater. 272–276, e1023 (2004).
9. J. L. Soubeyroux, D. Fruchart, C. Delmas, and G. Le Flem, J. Magn. Magn. Mater. 14, 159 (1979).
10. H. Kadowaki, H. Takei, and K. Motoya, J. Phys.: Condens. Matter 7, 6869 (1995).
11. M. Suzuki, I. Yamada, H. Kadowaki, and F. Takei, J. Phys.: Cond. Mat. 5, 4225 (1993).
12. S. Choi and A. Manthiram, J. Electrochem. Soc. 149(2), A162-A166 (2002).
13. manuscript in preparation.
14. Debye temperature, \(\theta \propto 1/(V^{1/3}M^{1/2})\) where \(V\) is the volume of the crystal unit cell and \(M\) is the molecular mass. Here in our case, higher molecular mass of LiCoO\(_2\) is almost neutralised by
the bigger volume of LiCrO$_2$ to get an expected ratio of Debye temperatures to be about 1.01.

15 P. Mendels et al., Private communication.

16 H. Kawamura and S. Miyashita, J. Phys. Soc. Jpn. **53**, 4138 (1984).

17 J.M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

18 J. M. Kosterlitz, J. Phys. C **7**, 1046 (1974).

19 V. L. Berezinskii, Sov. Phys. JETP **32**, 493 (1971).

20 P. Gaveau, J. P. Boucher, L. P. Regnault, and Y. Henry, J. Appl. Phys. **69**, 6229 (1991).

21 F. G. Mertens, A. R. Bishop, G. M. Wysin, and C. Kawabata, Phys. Rev. B. **39**, 591 (1989).

22 D. J. Bishop and J. D. Reppy, Phys. Rev. Lett. **40**, 1727 (1978).

23 M. Heinrich, H.-A. Krug von Nidda, A. Loidl, N. Rogado, and R. J. Cava, Phys. Rev. Lett. **91**, 137601 (2003).

24 D. L. Huber, Phys. Rev. B. **26**, 3758 (1982).

25 Y. Ajiro, H. Kikuchi, S. Sugiyama, T. Nakashima, S. Shamoto, N. Nakayama, M. Kiyama, N. Yamamoto, and Y. Oka, J. Phys. Soc. Jpn. **57**, 2268 (1988).

26 T. Moriya, Prog. Theor. Phys. **16**, 26 (1956).

27 N. Büttgen, A. Zymara, C. Kegler, V. Tsurkan, and A. Loidl, Phys. Rev. B. **73**, 132409 (2006).

28 M. Reehuis, A. Krimmel, N. Büttgen, A. Loidl, and A. Prokofiev, Eur. Phys. J. B **35**, 311 (2003).

29 Y. Ueda, N. Fujiwara, and H. Yasuoka, J. Phys. Soc. Jpn. **66**, 778 (1997).

30 B. D. Gaulin, J. N. Reimers, T. E. Mason, J. E. Greedan, and Z. Tun, Phys. Rev. Lett. **69**, 3244 (1992).

**Figure Captions**

FIG. 1 (Color online). XRD patterns of (a) LiCrO$_2$ and (b) Li$_{0.5}$CrO$_2$. Both the peak sets could be completely indexed using the space group $R3m$.

FIG. 2 (Color online). A schematic of the crystal structure of LiCrO$_2$.

FIG. 3 (Color online). Temperature dependence of bulk magnetic susceptibility ($M/H$) of LiCrO$_2$ and Li$_{0.5}$CrO$_2$ in an applied field of 1 T between 2 K to 300 K.

FIG. 4 (Color online). Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities for LiCrO$_2$ as a function of temperature between 2 K and 300 K in a field of 50 G. The plot shows a clear splitting of the ZFC and FC curves. The scatter in the data is due to the small magnetisation produced by a 50 G field which is near the limiting sensitivity of
FIG. 5 (Color online). Variation of $^7$Li NMR shift, $K(T)$ with temperature for LiCrO$_2$ above the region of transition temperature. Inset shows plot of $K$ versus bulk susceptibility, $\chi$ with temperature as an implicit parameter. From this plot, using Eq. (1), hyperfine coupling constant was estimated to be nearly 6 kG /$\mu_B$.

FIG. 6 (Color online). $^7$Li NMR FFT spectra of LiCrO$_2$ in the region of transition. Inset shows field sweep spectra at low temperatures 10 K and 4 K.

FIG. 7 (Color online). Temperature dependence of the $^7$Li NMR spectral intensity of LiCrO$_2$ obtained at 18 MHz between 4 K and 90 K. Here, echo integrated intensities have been corrected for temperature and $T_2$ effects. The error bar shown at 73 K is exemplary and indicates the value of error common to all the data points shown above 58 K. NMR signal was completely absent from 56 K to 35 K. The low-temperature points at 10 K and 4 K were obtained from the field- sweep spectra (cf. the inset of Fig. 6).

FIG. 8 (Color online). Temperature dependence of $^7$Li NMR spin-lattice relaxation rate, 1/$T_1$ for LiCrO$_2$ at $H = 1.08$ T. Solid line shown in the plot is fit of the relaxation data with Eq. (2) (discussed in section IV).

FIG. 9 (Color online). Variation of magnetic specific heat divided by temperature ($C_{mag}/T$) for LiCrO$_2$. $C_{mag}$ was obtained by subtracting the specific heat of non-magnetic LiCoO$_2$ (see text). Inset: Specific heat capacity versus temperature for LiCrO$_2$ and LiCoO$_2$. 
Fig. 1(a) and Fig. 1(b) show X-ray diffraction patterns with intensity (arb. units) plotted against 2θ (degree) for different crystallographic planes. The peaks at (003), (015), (104), and (110) are labeled for reference.
L. K. Alexander et al. Fig. 2
$\chi$ ($10^{-4}$ cm$^3$ / mol Cr)

T (K)

LiCrO$_2$

Li$_{0.5}$CrO$_2$

L. K. Alexander et al. Fig. 3
\( \chi (10^{-4} \text{ cm}^3 / \text{mol Cr}) \)

\[ T (\text{K}) \]

\[ H = 50 \text{ G} \]

L. K. Alexander et al. Fig. 4
$^7$Li NMR
$H = 1.08 \ T$

L. K. Alexander et al. Fig. 5
L. K. Alexander et al. Fig. 6
LiCrO$_2$
H=1.08 T

L. K. Alexander et al. Fig. 7
LiCrO$_2$

$H = 1.08$ T

$L. K. Alexander$ et al. Fig. 8
L. K. Alexander et al. Fig. 9