Possible Bose-Einstein condensate associated with an orbital degree of freedom in the Mott insulator CaCrO$_{3}$


DOI: 10.1103/PhysRevB.94.155137
A possible Bose-Einstein condensate associated with an orbital degree of freedom in the Mott insulator CaCrO₃

J.-S. Zhou¹*, L.-P. Cao², J.A. Alonso³, J. Sanchez-Benitez⁴, M.T. Fernandez Diaz⁵, X. Li¹,², J.-G. Cheng², L. Marshall¹, C.-Q. Jin², J.B. Goodenough¹,

¹ Materials Science and Engineering program/Mechanical Engineering, University of Texas at Austin, USA
² Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
³ Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28094 Madrid, Spain
⁴ Departamento de Quimica Fisica, Fac.CC. Quimicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain
⁵ Institute Laue-Langevin (ILL) 156X, F-38042 Grenoble Cedex 9, France

Whether CaCrO₃ is a Mott insulator or a correlated metal is still controversial. We have performed measurements of magnetization, specific heat, and thermal conductivity on CaCrO₃ samples selected from many batches of high-pressure synthesis. The single crystal CaCrO₃ sample exhibits an unprecedentedly sharp transition at a Néel temperature $T_N \approx 90$ K. The critical behavior of specific heat cannot be rationalized by the renormalization group theory for a second order magnetic transition. More surprisingly, the thermal conductivity $\kappa$ exhibits an anomalous drop on cooling through $T_N$, which is opposite to all known influence on $\kappa$ from either spin or orbital ordering. We have argued, on the basis of anomalies found in all three measurements and structural data, for the coexistence of itinerant $\pi$-bonding electrons in a $c$-axis band and localized $xy$ electrons in $xy$ orbitals responsible for type-C antiferromagnetic order below $T_N$ and the occupation of a pure, localized $xy$ orbital undergoing a Bose Einstein condensate (BEC) at $T_N$. 

The perovskite CaCrO$_3$ has drawn considerable attention in recent years.$^{1-8}$ The available experimental results of this perovskite are still controversial. An early-day study on a crystal grain showed a metallic conduction to the lowest temperature with a small jump of resistivity on cooling through $T_N$. For polycrystalline samples, a high and activated resistivity was found.$^5$ However, an optical study on polycrystalline samples showed a finite conductivity at $\omega = 0$, which is evidence for a metal.$^{4,5,7}$ On the other hand, neutron diffraction on a CaCrO$_3$ sample has revealed an evolution of a local structural change as a function of temperature and a type-$C$ antiferromagnetic ordering below $T_N \approx 90$ K.$^{4,5}$ The finding of a collinear type-$C$ antiferromagnetic ordering, typical for localized electrons, contradicts the conclusion of itinerant electrons from the reflectivity measurement. The local structural distortion also reflects an unusual electronic state and unprecedented orbital dynamics. The orthorhombic $Pbnm$ perovskite has intrinsic distortions that can be extracted from isostructural CaTiO$_3$ and CaVO$_3$ where orbital ordering is not an issue.$^{10,11}$ The intrinsic distortions bias the orbital ordering in orbitally degenerate systems such as in the $t_2$ electronic systems of RTiO$_3$ (R=rare earth, and Y).$^{12,13,14}$ Neutron diffraction$^5$ showed that an orbital degeneracy survives through a magnetic transition and to lower temperatures. The analysis of critical phenomena of physical properties and an unusual thermal conductivity at $T_N$ indeed reveal new physics associated with the interaction between spins and orbital dynamics. We argue that while the orbital degeneracy is not removed, a giant number of collective orbital excitations undergo a Bose-Einstein condensate on cooling through the Néel temperature in CaCrO$_3$.

The CaCrO$_3$ samples were made under high pressure. Large cubes (100 ~200 $\mu$m) of CaCrO$_3$ crystal can be found in some batches of the high-pressure products. Measurements of physical properties were performed on single-crystal samples, polycrystalline samples with embedded crystal grains, and on uniformly polycrystalline samples. Detailed information about the samples’ preparation, characterization and measurements of physical properties can be found in the Supplementary Information (SI).$^{15}$ Fig.1 shows the result of a magnetization measurement on a single crystal sample; the transition at $T_N$ is remarkably sharp. In type-$C$ ordering, the easy magnetization axis is along the $\pm y$ direction of the orthorhombic cell according to neutron diffraction studies.$^{4,5}$ For the $Pbnm$ crystal structure, the compatible magnetic structure is $F_xC_y$ of the irreducible representation $\Gamma_2$.$^{16}$ However, it is impossible for neutron diffraction to pick up a tiny spin canting in the $x$ direction. By considering the interatomic spin-orbit coupling, Moriya
has put forward the theory of antisymmetric spin coupling in localized magnetic insulators that
gives a quantitative description of spin canting and the temperature-dependent magnetization.
The magnetic susceptibility for the field perpendicular to the easy axis is expressed as
\[ \chi = \frac{N g^2 \mu_B^2 S(S + 1)}{3k(T + T_N)} \frac{T - T_0}{T - T_N}, \quad T_N = \frac{JZS(S + 1)}{3k} \left[ 1 + \frac{D}{J} \right]^{1/2}, \quad T_0 = \frac{JZS(S + 1)}{3k} \]
where \( Z \) is the number of nearest neighbors and \( D \) is the Dzialoshinski-Moryia coupling
constant. In contrast to a regular antiferromagnet, the susceptibility for the AF system with
canted spins would exhibit an extremely sharp transition at \( T_N \). The transition area of
magnetization data in Fig.1 can be fit to the expression very well; the fitting gives a \( D \approx 4 \) K and
a spin canting angle \( \theta \approx 0.08^\circ \) based on \( \tan 2\theta \sim D/2J \) from the theory. In comparison, a metallic
antiferromagnet Nb\(_{12}\)O\(_{29}\) shows a broad peak at \( T_N \) in the temperature dependence of
magnetization.\(^{18}\) It should be stressed that the antisymmetric exchange interaction has been
found only in localized-electron antiferromagnets.

As shown in Fig.1, the transition at \( T_N \) in the polycrystalline samples is relatively broad. A
transition at a lower temperature or multiple transitions can also be identified in the results of
specific heat measurements in these samples. A lower \( T_N \) is related to oxygen non-stoichiometry
in the samples.\(^5\) Fig.2(a) shows the \( C_p \) of crystal cubes and the polycrystalline samples
with/without embedded crystals. The Néel temperature \( T_N \) of these samples can be obtained from
a \( \lambda \)-shape anomaly in the plot of \( C_p \) versus temperature. The single crystal sample exhibits the
highest \( T_N \) among samples studied. As characterized by SEM in SI,\(^{15}\) sample A is a uniformly
polycrystalline sample, which shows a much broader transition at a relatively lower temperature.
Sample B, a polycrystalline sample with a few embedded crystals, shows a slightly higher \( T_N \)
than that of sample A and an anomaly at the temperature corresponding to \( T_N \) of the single
crystal sample is also visible. Embedded crystals in sample C occupy more than 1/3 of the
sample’s volume. A \( \lambda \)-shape anomaly is essentially the same as that at \( T_N \) in the single crystal
sample, but the magnitude is lower. All these observations demonstrate that all single-crystal
grains found in different batches of high pressure synthesis have the same \( T_N \) that is higher than
the broad anomaly at \( T_N \) in polycrystalline samples.
The magnetic contribution $C_m$ to the specific heat in Fig.2(a) of single crystal CaCrO$_3$ was obtained by subtracting the lattice contribution obtained by fitting $C_p(T)$ with a combination of the Debye and Einstein formulae at temperatures away from the vicinity of $T_N$. The $C_m(T)$ versus the reduced temperature $t = (T-T_N)/T_N$ has been compared directly with a $C_m(T)$ of typical Heisenberg magnets. The transition at $T_N$ for a single-crystal CaCrO$_3$ is significantly narrower than that for a regular second-order magnetic transition. One may be curious whether the super-sharp anomaly at $T_N$ in CaCrO$_3$ is simply caused by a first-order transition. The structural study indicated that there is no volume change. As shown in the SI, a spike with extremely high magnitude and a discontinuity of $C_p$ caused by latent heat at the first-order transition in LuVO$_3$ clearly distinguish the $C_p(T)$ found in CaCrO$_3$ from a first order transition. More importantly, a first-order transition does not come with critical fluctuations. For a second-order magnetic transition, the critical behavior can be described by a power law based on the renormalization group theory. The $C_m$ data are well-mapped along two parallel lines in the plot of $\log C_m$ versus $\log[1-T/T_N]$ near $T_N$ in Fig.2(b), which indicates that the critical behavior of CaCrO$_3$ can be perfectly described by a power law. However, the exponent obtained by linear fitting the plot is $\alpha^+ = -0.75(3), \alpha^- = -0.75(2)$ for the data above and below $T_N (= 89.089 \text{ K})$, which is significantly different from an $\alpha = -0.11$ for a 3D Heisenberg magnet and actually different from any exponents for a variety of magnetic models. On the other hand, $C_m(T)$ of the CaCrO$_3$ crystal shares stunningly the essential feature of the $C_v$ of $^4\text{He}$ at the $\lambda$ transition from $^4\text{He}$ I to $^4\text{He}$ II. The quantum liquid of $^4\text{He}$ undergoes a Bose-Einstein condensation (BEC) into the superfluid phase of $^4\text{He}$ II. In the case of the quantum spin-dimer system Sr$_3$Cr$_2$O$_8$, an extremely sharp anomaly has also been found where the applied magnetic field $H$ is well above a critical value $H_c$ of the quantum critical point. While the spin ordering state is no different from that of a Néel state, the magnetic transition and its field dependence associated with a degenerate state for triplons can be treated by a BEC. In addition to the sharp anomaly, the critical exponents for a BEC are normally different from those predicted by the renormalization group theory. For example, at the $\lambda$ transition of $^4\text{He}$, a $C_v = -\alpha\ln[(T_c-T)/T_c] + b$ has been reported instead of the power law. In the case of the BEC in Sr$_3$Cr$_2$O$_8$, an $\alpha \approx - 0.3$ was obtained by analyzing the data in ref.22. Generally speaking, a small temperature range $t_G$ for critical fluctuations means a longer coherence length $\xi_0$ based on the Ginzburg criterion $t_G = (T_G-T_c)/T_c \sim \Delta C^{-2}\xi_0^{-1}$, where $\Delta C$ is the jump of $C_m$ at $T_c$ or $T_N$. A smaller $t_G$ is consistent with a condensation-type transition.
where macroscopic occupation of a quantum state occurs. This analysis together with the anomalous $\alpha$ implies that the CaCrO$_3$ crystal may actually undergo a BEC near 90 K.

The thermal conductivity $\kappa$ reveals the dynamics of spins, lattice, and orbitals, which could give an important clue of what happens at $T_N$ in CaCrO$_3$. Fig.3 shows the results of thermal conductivity measurements made on polycrystalline CaCrO$_3$ samples. It is impossible for us to measure the thermal conductivity on a 200 $\mu$m grain of CaCrO$_3$ crystal. However, measurements made on the sample C help to isolate a $\kappa(T)$ that is essentially from the single crystal CaCrO$_3$; see SI$^{15}$ for detailed information. A small and weak temperature dependence of $\kappa$ is found for both polycrystalline and single crystal CaCrO$_3$ samples over a broad temperature range above $T_N$. The $\kappa(T)$ of CaCrO$_3$ is located between two extreme oxide cases, *i.e.* an amorphous oxide and a LaGaO$_3$ crystal. The LaGaO$_3$ crystal serves as an example of phonon thermal conductivity since it is a diamagnetic insulator. On the other hand, the minimum thermal conductivity $\kappa_{\text{min}}$ can be calculated from an amorphous oxide in which the mean-free path is not longer than the interatomic distance. The $\kappa$ of CaCrO$_3$ is close to a phonon thermal conductivity in magnitude near room temperature; but the temperature dependence is characteristic of an amorphous oxide.

The thermal conductivity in a solid is described by $\kappa = \frac{1}{3}C\nu\ell$, where $C$ is the specific heat, $\nu$ the acoustic sound velocity and $\ell$ the mean free path. In a glass, the temperature dependence of $\kappa$ is dominated by the $C$ since the $\ell$ for short-range phonons is small.$^{27}$ The $\kappa$ of CaCrO$_3$ resembles the temperature dependence of $C_p$ since $\ell$ is a constant in this amorphous-like oxide.

The magnetic transition at $T_N$ causes an abrupt drop of $\kappa$, which is clearly observed in sample C. However, the drop is diminished in the sample A and B as shown in the inset of Fig.3(a). An amorphous-like $\kappa(T)$ has been seen in other crystalline oxides with an orbital degeneracy. However, a further reduction from the amorphous-like $\kappa$ of CaCrO$_3$ on cooling through $T_N$ is highly unusual.

Inverse $\kappa$ versus temperature of several Mott insulators are plotted in Fig.3(b). Each of them offers different stories of how magnetic ordering and orbital ordering influence the thermal conductivity. YCrO$_3$ has no orbital degeneracy and exhibits type-G AF ordering at $T_N$. The $\kappa(T)$ of YCrO$_3$ in the paramagnetic phase resembles that of LaGaO$_3$. The $\kappa$ increases on cooling through $T_N$ because of the magnon contribution and reduced scattering between spin excitations.
and phonons in the magnetically ordered phase. YVO₃ has the same electronic configuration, i.e. $t^2_e e^0$ as that of CaCrO₃; however, the orbital degeneracy in YVO₃ survives only down to 180 K. Orbital fluctuations contribute a glassy $\kappa$ for $T > 180$ K. At the orbital ordering transition $T_{OO}$, the $\kappa$ bottoms out. A phonon-like $\kappa$ is restored at $T < T_{OO}$ since a long periodicity in the lattice is established due to the orbital ordering. On cooling through $T_N < T_{OO}$, YVO₃ experiences a spin disorder-order transition where the $\kappa$ is further enhanced. A phonon $\kappa$ is finally realized through a first order transition at $T_{CG} < T_N$. In LaTiO₃, the orbital degeneracy survives in the entire temperature range of the paramagnetic phase. On cooling through $T_N$, the spin/orbital ordering restores the phonon-like thermal conductivity. These experiments clearly reveal how sensitive the thermal conductivity is as a probe for spin and orbital orderings and show a general trend that orbital ordering and spin ordering restore thermal conductivity. While a glassy $\kappa$ in the paramagnetic phase of CaCrO₃ is clearly related to the orbital degeneracy, the sharp drop of $\kappa$ on cooling through $T_N$ distinguishes CaCrO₃ from any oxide systems studied so far. Critical fluctuations would cause a small dent around a magnetic transition temperature, i.e. a small drop and then a coming back of $\kappa$; see the data for CoF₂ for example. But the influence of critical fluctuations on the thermal conductivity is fundamentally different from what happens at $T_N$ in CaCrO₃. After exhausting all possible consequences of spin/orbital ordering, we focused on whether a BEC can account for the observed drop in $\kappa$ on cooling through $T_N$.

As interacting Bose particles condense, it is acknowledged that condensed particles carry no entropy and make no contribution to the thermoelastic properties. Condensed particles normally represent a very small fraction of all particles in a real system. As a result, the impact to the thermal conductivity from condensed particles is negligible compared to that from normal particles. In $^4$He, a five-order jump of $\kappa$ occurs on cooling through the $\lambda$ point. In all quantum spin systems, the magnetic state below $T_N$ is not different from a classic Néel state. A jump of $\kappa$ due to the magnon contribution on cooling through $T_N$ has always been found in these quantum spin systems. On the other hand, in heavy metal superconductors like Pb, for example, electrons in states within a range of $kT$ around the Fermi energy are dominant heat carriers. As these electrons form Cooper pairs and condense at $T < T_c$, the $\kappa$ drops, which demonstrates that condensed Bose particles carry no entropy.
In order to find possible particles/quasiparticles in CaCrO$_3$ that condense at T$_N$, we start from the local crystal structure since it reflects the electron and the orbital state. CrO$_6$ octahedra in CaCrO$_3$ are slightly compressed, \( i.e. \ c/a < 1 \), at room temperature.$^5$ This local site distortion is contrary to the intrinsic distortions in a \( Pbnm \) perovskite structure that would bias an orbital ordering leading to long, medium, and short Cr-O bonds.$^{13,14}$ A compressed CrO$_6$ octahedron is compatible with the orbital occupation of \( xy \ (l_z=0) \) and \( yz\pm izx \ (l_z = \pm 1) \) for a \( t^2_2 \) electron manifold. The spin-orbit coupling would make the spin easy axis along the \( c \) direction if the orbital angular momentum is not quenched. The observation of an easy magnetic axis along the \( b \) axis,$^5$ however, indicates that the orbital angular momentum is fully quenched. Moreover, an abrupt collapse of the Cr-O bond length along the \( c \) axis and an expansion in the \( ab \) plane on cooling through T$_N$ in a type-C antiferromagnet are just opposite to what would be predicted for a localized-electron magnetostrictive distortion. We are, therefore, forced to conclude that, at least below T$_N$, there are itinerant \( yz, zx \) electron in a narrow \( c \)-axis \( \pi^* \) band that is ¼-filled, which is consistent with ferromagnetic \( c \)-axis coupling of the localized \( xy \) spins that are antiferromagnetically coupled in the basal plane. Although the Cr-O bond lengths as well as the lattice parameters (excluding the volume) changes abruptly at T$_N$, the magnetic ordering and the \( c/a \) changes leave the transition second-order as indicated by the critical fluctuations seen in the specific-heat data. Since a classic orbital ordering is not an option here, we turn to the possibility that the \( xy \) orbital occupation undergo a BEC to account for the drop in the \( \kappa \) on cooling through T$_N$.

Whether particles can undergo a BEC depends critically on number conservation.$^{23}$ In a typical orbitally ordered phase, as is found in the paramagnetic phase of LaMnO$_3$ below 750 K, the orbital excitations are described as orbitons.$^{38}$ The number of orbitons is not conserved. Analogous to quantum magnets where a BEC causes a sharp increase of magnetization, the Bose density in CaCrO$_3$ corresponds to the \( a/c \) ratio of an octahedron. The \( xy \) orbital occupation and/or localization leads to abrupt expansion of the \( ab \) plane and increase of \( a/c > 1 \). Thermal vibrations involve all possible atomic displacements allowed by the crystal symmetry, which include modes associated with the orbital occupation. In quantum magnets,$^{33-36}$ heat flux carried by magnetic excitations is negligible in compared to that by lattice vibrations. A jump of \( \kappa \) at T$_c$ may reflect the influence of a BEC to the lattice. In CaCrO$_3$, however, the lattice vibrations associated with
the xy orbital occupation no longer contribute to the $\kappa$ at $T \leq T_N$. A slightly smaller $C_p$ of the crystal sample than that of polycrystalline samples at $T < T_N$, see the inset of Fig.2(a), may indicate fewer degrees of freedom available for heat carriers. The analysis of thermal conductivity is highly consistent with a possible BEC from the critical behavior of $C_p$. The extremely sharp magnetic transition in single crystal CaCrO$_3$ may be interpreted on the basis of a BEC. As a matter of fact, the BEC model for TlCuCl$_3$ predicts an abrupt jump of magnetization on cooling through $T_c$.

In summary, oxygen-stoichiometric single-crystal CaCrO$_3$ exhibits three unprecedented features: (1) localized and itinerant electrons coexist in $\pi$-bonding $t_2$ orbitals on the same atom in the structure, (2) the bias effect by the intrinsic distortion in the $Pbnm$ perovskite structure is entirely overwhelmed by the coexistence of itinerant yz, zx electrons and localized xy electrons, (3) a drop in thermal conductivity on cooling through $T_N$. We believe the experimental data manifest a BEC at $T_N$ in CaCrO$_3$. A BEC of the orbital occupation accounting for (3) relies largely on the peculiar electron and orbital status in (1) and (2).

Acknowledgment

This work was supported by the National Science Foundation (DMR MIRT 1122603) and the Robert A Welch Foundation, Houston, Texas in the US. JAA, RMC, JSB, and MTF thank the Spanish MINECO project MAT2013-41099-R and RyC-2010-06276 for financial support. JSZ is grateful for the enlightening discussions with V. Zapf and S. Chernyshev.

*jszhou@mail.utexas.edu

References

1. B.L. Chamberland, Solid State Commun. 5, 663 (1967)
15. Detailed information about sample’s synthesis and characterization, structural refinement and parameters, measurement of the thermal conductivity, the analysis of specific heat.
17. T. Moriya, Phys. Rev. 120, 91 (1960)
32. F. Pobell, Matter and Methods at Low Temperatures, p23 (Springer Berlin 2007)
Fig. 1 Temperature dependence of magnetization for (a) single crystal and (b) polycrystalline samples of CaCrO$_3$. 

H = 1000 Oe
Fig. 2 (a) Temperature dependence of specific heat for a variety of CaCrO$_3$ samples; the inset: a zoom-in plot of the transition area; (b) the magnetic contribution $C_m$ versus reduced temperature $(T-T_c)/T_c$ for CaCrO$_3$, Heisenberg magnets, and the $\lambda$ transition in $^3$He for comparison.
Fig. 3. (a) Temperature dependence of thermal conductivity for a variety of CaCrO$_3$ samples and LaGaO$_3$ crystal; inset: a zoom-in plot of the transition area of the CaCrO$_3$ samples; a solid line inside the data of LaGaO$_3$ represents the fitting result to the Boltzmann formula; (b) the inverse thermal conductivity versus temperature for a CaCrO$_3$ sample and YVO$_3$, YCrO$_3$, and LaTiO$_3$ for comparison.