CaCrO$_3$: an anomalous antiferromagnetic metallic oxide

A. C. Komarek,$^1$ S. V. Streltsov,$^2$ M. I. Isobe,$^3$ T. Möller,$^1$ M. Hoedel,$^4$ A. Senyshyn,$^4$ D. Trots,$^5$ M. T. Fernández-Díaz,$^6$
T. Hansen,$^6$ H. Gotou,$^3$ T. Yagi,$^3$ Y. Ueda,$^3$ V. I. Anisimov,$^2$ M. Grüniger,$^1$ D. I. Khomskii,$^1$ and M. Braden$^1$

$^1$II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Köln, Germany
$^2$Institute of Metal Physics, S. Kovalevskoj St. 18, 620041 Ekaterinburg GSP-170, Russia
$^3$Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
$^4$Technische Universität Darmstadt, Material und Geowissenschaften, Petersenstrasse 23, D-64287 Darmstadt, Germany and Technische Universität München, FRM-II, Lichtenbergstr. 1, D-85747 Garching, Germany
$^5$Hasylab/DESY, Notkestr. 85, D-22607, Hamburg, Germany
$^6$Institut Laue-Langevin, 38042 Grenoble, France

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Combining infrared reflectivity, transport, susceptibility and several diffraction techniques, we find compelling evidence that CaCrO$_3$ is a rare case of a metallic and antiferromagnetic transition-metal oxide with a three-dimensional electronic structure. LSDA calculations correctly describe the metallic behavior as well as the anisotropic magnetic ordering pattern of $C$ type: The high Cr valence state induces via sizeable $pd$ hybridization remarkably strong next-nearest neighbor interactions stabilizing this ordering. The subtle balance of magnetic interactions gives rise to magneto-elastic coupling, explaining pronounced structural anomalies observed at the magnetic ordering transition.

Strongly correlated electron systems including the wide class of transition-metal oxides exhibit a quite general relation between magnetic order and electrical conductivity [1]: ferromagnetism typically coexists with metallic conductivity, whereas insulators usually exhibit antiferromagnetism. It is always a challenge to understand exceptions from this rule. The rare observations of ferromagnetism in insulating transition-metal oxides most often are due to a particular type of orbital ordering [2]. The few examples of antiferromagnetic (AFM) metals, e.g., (La/Sr)$_3$Mn$_2$O$_7$ [3] or Ca$_3$Ru$_2$O$_7$ [4], are characterized by reduced electronic and structural dimensionality, and the antiferromagnetic order corresponds to a stacking of ferromagnetic (FM) layers. Here we report the discovery of a three-dimensional transition-metal oxide with metallic conductivity, antiferromagnetic exchange interactions, and $C$-type antiferromagnetic order: the perovskite CaCrO$_3$.

Perovskites containing Cr$^{4+}$ (CaCrO$_3$, SrCrO$_3$, and PbCrO$_3$) were already studied previously [3, 4, 7, 8, 9, 10], but neither the details of the crystal structure nor the nature of the magnetic ordering are known. Only very recently evidence for $C$-type AFM order was reported in multi-phase samples of SrCrO$_3$ [10]. Regarding the conductivity, the existing data are controversial. In Refs. [7, 8] CaCrO$_3$ was claimed to be metallic, but more recently insulating behavior has been reported [2]. A similar controversy persists also for SrCrO$_3$, which should definitely be more metallic than CaCrO$_3$ due to the less distorted crystal structure, but metallic behavior was observed in Ref. [5] only under pressure. These controversies most likely are connected with the difficulty to prepare high-quality stoichiometric materials and with the lack of large single crystals.

CaCrO$_3$ exhibits an orthorhombic GdFeO$_3$-type perovskite structure and early magnetization measurements indicate a magnetic transition at 90 K [8], which is confirmed in our samples. Two electrons occupy the Cr 3d shell (S=1), rendering the material electronically similar to insulating RVO$_3$ [11] (also 3d$^2$) and to metallic (Ca/Sr)RuO$_3$ (4d$^2$) [12]. CaCrO$_3$ shows an unusually high transition-metal valence, Cr$^{4+}$, which may lead to a small or even negative charge-transfer gap [13, 14], i.e., holes in the O band. In CrO$_2$ with rutile structure and edge-sharing CrO$_5$ octahedra, the negative charge-transfer gap leads to self-doping [15] and to the appearance of a ferromagnetic metallic state. In contrast, the layered perovskite Sr$_2$CrO$_4$ with corner-sharing octahedra and $\sim 180^\circ$ Cr-O-Cr bonds is an AFM Mott-Hubbard insulator with a gap of about 0.2 eV [10].

Combining diffraction, macroscopic and infrared reflectivity measurements with LSDA as well as with LSDA+U calculations we have studied the properties of CaCrO$_3$. We find that CaCrO$_3$ is an antiferromagnetic metallic transition-metal oxide with a $C$-type magnetic structure. According to LSDA calculations, the magnetic order arises from competing nearest-neighbor (nn) and next-nearest-neighbor (nnn, ”diagonal”) exchange interactions, which result from a sizeable $pd$ hybridization. Remarkably, the magnetic transition at T=90 K causes pronounced anomalies in structural and transport properties.

Polycrystalline CaCrO$_3$ was prepared by a solid state reaction of CaO and Cr$_2$O$_3$ under 4 GPa at 1000°C for 30 minutes. The obtained samples of stoichiometric reactions always include a varying amount of the impurities of Cr$_2$O$_3$ and CaCr$_2$O$_4$. This impurity problem has also been reported by Goodenough et al. [8]. A small excess of CaO (5-10%), however, almost completely eliminated these impurities, and the excess CaO could be washed out with distilled water. Close inspection showed that single-crystalline grains of up to 0.1 mm diameter were...
obtained by this procedure as well. Powder neutron measurements were performed on the SPODI diffractometer at the FRM-II reactor ($\lambda = 1.548\text{Å}$) as well as on the D20 high-flux diffractometer at the ILL ($\lambda = 2.4233\text{Å}$). Lattice parameters have been studied with synchrotron radiation at the beamline B2 at Hasylab/DESY ($\lambda = 0.75\text{Å}$) using an image plate detector for temperatures between 15 K and 1063 K. At about 710 K a starting sample decomposition, however, allowed us to obtain reliable data only up to $\sim 800$ K. X-ray single-crystal structure analysis was performed on a Bruker X8-Apex diffractometer using Mo-K$_\alpha$ radiation between 90 K and 300 K. Although the sample showed a superposition of six different twin-domain orientations, a satisfactory intensity integration was achieved due to the low splitting of the pseudo-cubic parameters. Final R-values referring to the intensities were between 2 and 4%. This experiment confirms the close to perfect stoichiometry of our samples. The electrical resistivity $\rho(T)$ was measured by an AC four-point method on a pellet of CaCrO$_3$ powder which was cold-pressed at 12.5 kbar. The infrared reflectivity $R(\omega)$ of a cold-pressed pellet was determined between 7 meV and 0.9 eV using a Bruker IFS 66v/S Fourier-transform spectrometer. For the reference measurement we used in-situ Au evaporation. The real part $\sigma_1(\omega)$ of the optical conductivity has been obtained via a Kramers-Kronig analysis, for which $R(\omega)$ has been extrapolated to lower and higher frequencies using a conventional Drude-Lorentz fit.

The lattice parameters of CaCrO$_3$ determined by synchrotron-radiation powder diffraction are shown in Fig. 1. All three orthorhombic parameters exhibit a step-like anomaly at the magnetic ordering temperature determined by the SQUID susceptibility and neutron diffraction measurements, $T_N$=90 K. Although the sudden changes in the lattice constants are rather strong, up to 0.5% for $c$, there is no visible effect in the lattice volume. Whereas $c$ shrinks, $a$ and $b$ elongate upon cooling, yielding a flattening of the $Pbnm$ structure. We emphasize that there is no evidence for phase mixture apart very close to $T_N$. Close inspection of the temperature dependence suggests that this lattice flattening already starts at much higher temperatures.

The neutron powder and the x-ray single-crystal experiments give the full structural information including the positional and the displacement parameters, from which all bond angles and distances can be calculated. The results are given in Fig. 2. The GeFeO$_3$-type structure (space group $Pbnm$) develops out of the ideal perovskite structure by rotating, angle $\Phi$, and tilting, angle $\Theta$, the CrO$_6$ octahedra. Between 3.5 and 300 K, $\Theta = 10.5^\circ$ and $\Phi = 8.2^\circ$ are nearly constant, reflecting a sizeable structural distortion. The combination of tilt and rotation yields two distinct O positions: apical O1 out-of-plane and O2 in the $ab$ plane. Regarding a distortion of the basal plane of the octahedron, we do not find a splitting in the Cr-O2 distances but a weak temperature independent elongation of the octahedron parallel to $a$, i.e. the O2-O2 edges are different (see Fig. 2). In addition, we find an overall flattening of the octahedron following the flattening of the lattice at $T_N$: The Cr-O1 (Cr-O2) distance shrinks (elongates) upon cooling. The compression of the octahedron points to a temperature-driven redistribution amongst the $t_{2g}$ orbitals increasing the $d_{xy}$ occupation upon cooling into the magnetically ordered state. In electronically similar Ca$_2$RuO$_4$, a similar flattening of the octahedron has been attributed to a pronounced orbital rearrangement [18, 19], but there the effects are about an order of magnitude larger than in CaCrO$_3$.

Below $T_N$=90 K two strong magnetic peaks emerge at (100) and (102)/(012) which can unambiguously be attributed to $C_y$-type AFM order, see Fig. 2. Other schemes do not yield the correct peak positions or fail to describe the intensity ratio. In space group $Pbnm$ the $C_y$-type order may couple with $F_x$ and $G_z$ components according to the irreducible representation $\Gamma_{2g}$ [20]. The $F_x$ component perfectly agrees with the observation of weak ferromagnetism in the susceptibility, see Fig. 2b). We find a sizeable ordered moment of 1.2$\mu_B$ at low temperature, which, however, is much below the expected value for a $S=1$ moment.

The resistivity $\rho(T)$ exhibits $\partial \rho / \partial T < 0$ and a rather small value at 300 K, 0.1$\Omega$m (see inset of Fig. 3). Furthermore, $\rho(T)$ does not diverge towards low $T$ but tends to a finite value. Upon a first cooling cycle we find a clear jump at $T_N$ most likely due to cracks caused by the pronounced structural anomalies. A similar jump was observed close to 90 K in $\rho(T)$ of a metallic single crystal [8], suggesting that this sample exhibits a fully comparable magnetic transition and thus can be considered to represent stoichiometric CaCrO$_3$. But $\rho(T)$ of polycrystalline CaCrO$_3$ appears to be dominated by grain boundaries.

In contrast to DC transport, optical data can reveal the metallic properties of a polycrystalline metal with insulating grain boundaries. Figure 3 clearly demonstrates
FIG. 2: (color online) a) Crystal structure of CaCrO$_3$ in space group Pbnm and the C-type magnetic structure of Cr moments (red) indicating the main magnetic interaction paths. b) Magnetic susceptibility. c–h) Results of powder neutron (squares) and single crystal X-ray (circles) measurements. c): Magnetic (010)/(100) reflection at 3.5 K and calculated profiles for $C_x$, $C_y$ and $C_z$ type magnetic order. d): Part of the neutron diffraction pattern at 3.5 K and calculated profiles. e): Ratio of O2-O2 and Cr-O2 bond lengths; f): Octahedral tilt $\Theta$ and rotation $\Phi$ angles. g): Cr-O1 and Cr-O2 bond lengths. h): $C_y$-type ordered magnetic moment in $\mu_B$.

that CaCrO$_3$ is a metal with a moderate conductivity, $\sigma_1(\omega)$ of the order of a few hundred to 1000 ($\Omega cm$)$^{-1}$. Typical for a metal, $R(\omega)$ extrapolates to 1 for $\omega \to 0$. Phonons are observed between 20 and 80 meV, and in $R(\omega)$ they are strongly screened by the itinerant charge carriers. However, the frequency dependence deviates strongly from a typical Drude behavior. The spectral weight is almost entirely dominated by a peak at about 350 meV. An increase of $\sigma_1(\omega)$ with decreasing frequency is recovered only below 30 meV at 20 K. Although $\sigma_1(\omega)$ appears to be dominated by excitations with finite frequency, we emphasize that $R(\omega)$ unambiguously demonstrates the presence of free carriers. This further agrees with the magnetic susceptibility which, above $T_N$ is very small and hardly temperature dependent indicating itinerant magnetism, see Fig. 2b).

In the case of insulating grain boundaries, $\sigma_1(\omega)$ is suppressed at low frequencies. However, this can not explain the peak observed at 350 meV. Since a wavelength of $\lambda = 20 \mu m$ is equivalent to a photon energy of $\sim 60$ meV, grain-size effects can become important only much below 350 meV [21]. We attribute the peak at 0.35 eV to excitations from the lower (LHB) to the upper (UHB) Hubbard band. Due to the high valence of Cr$^{4+}$, the Cr Hubbard bands shift down towards the fully occupied O-2p band, whereas the $pd$ hybridization between Cr and O bands pushes the LHB back upwards, reducing the effective Coulomb repulsion $U_{\text{eff}}$ [22] and admixing O-2p states to the LHB and the UHB in the same way as it was demonstrated for CrO$_2$ [15]. In insulating Sr$_2$CrO$_4$ with Cr$^{4+}$ in a $d^2$ configuration [16], this LHB-UHB excitation was observed at 1.0 eV. Integrating $\sigma_1(\omega)$ from 7 meV to 0.9 eV in CaCrO$_3$ yields an effective carrier density $N \approx 0.1$ per Cr ion. Remarkably, this is very similar to the spectral weight of the LHB-UHB peak in Sr$_2$CrO$_4$ [16]. From a conventional Drude-Lorentz fit we estimate that the spectral weight of the free-carrier Drude contribution is about 5% of the total weight at 20 K. Apparently, CaCrO$_3$ is very close to localized-itinerant crossover. Its metallic behavior compared to insulating Sr$_2$CrO$_4$ should be a consequence of the three-dimensional crystal structure inducing larger band widths and thus smaller $U_{\text{eff}}$.

To further analyze the electronic structure, we carried out ab-initio band structure calculations for the T=3.5 K crystal structure within the LSDA approximation using the linear muffin-tin orbitals method [23]. Exchange constants were computed from the total energies of different magnetic solutions, using the crystal structure presented.
above. In LSDA, CaCrO$_3$ is metallic in all studied magnetic structures: FM, AFM-G (all nn spins antiparallel), AFM-A (AFM coupled FM $ab$ planes) and two AFM-C types with FM chains running in different directions. In agreement with experiment, the AFM-C structure with FM chains running along $c$ exhibits the lowest energy. The calculated magnetic moment is $\mu = 1.52\mu_B$/Cr, in good agreement with the measured value of $1.2\mu_B$. The reduction from $2\mu_B$ expected for Cr$^{4+}$ ($S = 1$) is caused by the strong $pd$ hybridization.

Studying the exchange parameters allows one to understand the apparently anisotropic magnetic structure. We find a strong AFM interaction between nn spins within the $ab$ plane, $J = 80$ K, for the notation of magnetic interactions see Fig. 2a). Surprisingly, also the nn exchange along $c$ is AFM and only slightly smaller, $J' = 60$ K, although the experiment finds FM coupling in this direction. Its cause resides in a remarkably strong AFM nn interaction along the diagonal, $J'' = 33$ K. Since $J' < 4J''$, the AFM $J''$ is overruled yielding the C-type structure. Thus, the anisotropic magnetic structure develops due to strong and anisotropic nn interactions despite nearly isotropic nn interactions. Also the diagonal nn exchange within the $ab$ planes is AFM, $J''_{ab} = 22$ K, but not sufficient to overrule the nn $J$. The subtle balance of different interactions may give rise to strong magnetoeelastic coupling, explaining the pronounced structural anomalies at $T_N$. The flattening of the octahedron enhances the $d_{xy}$ occupation thereby increasing $J$ and - more importantly - decreasing $J'$. Note that magnetic interactions in the LSDA approach are due to the band magnetism of itinerant electrons. Therefore, the rather large diagonal coupling parameters are caused by strong $pd$ hybridization.

To check the importance of electronic correlations, we also performed LSDA+$U$ calculations with on-site Coulomb interaction $U = 3$ eV and Hund’s rule coupling $J_H = 0.87$ eV. Also in LSDA+$U$ the ground state is C-type AFM, but the electronic state is very different. In LSDA+$U$, CaCrO$_3$ is an insulator with a gap of $E_g \sim 0.5$ eV (note that LSDA+$U$ tends to overestimate $E_g$). In the LSDA+$U$ approach, the C-type magnetic structure is associated with orbital ordering: one electron localizes in the $xy$ orbital at each Cr site and provides the in-plane AFP interaction, the second electron occupies alternating $1/\sqrt{2}(xz + yz)$ and $1/\sqrt{2}(xz - yz)$ orbitals. According to the Goodenough-Kanamori-Anderson rules this causes a FM interaction along $c$. This state is very similar to the one reported for insulating YVO$_3$ with G-type orbital order causing C-type magnetism. We have searched for the orbital-order superstructure reflections in CaCrO$_3$ by high-flux powder neutron diffraction but did not find them although superstructure reflections $10^3$ times weaker than a strong fundamental reflection would have been observed. Furthermore, a free refinement of the orbital-order model with the high resolution SPODI data does not yield any evidence for orbital ordering. We may thus exclude an orbital order comparable to that in YVO$_3$ for CaCrO$_3$. LSDA+$U$ evidently does not describe CaCrO$_3$ properly, but we nevertheless think that electronic correlations are important in CaCrO$_3$ driving it close to a metal-insulator cross-over.

Summarizing our comprehensive investigation, combining diffraction, macroscopic and optical studies, we conclude that CaCrO$_3$ is a metallic and antiferromagnetic transition-metal oxide. There are other metal-ferromagnetic oxides known, but these exhibit a reduced electronic and structural dimensionality rendering CaCrO$_3$ unique. The anisotropic C-type magnetic structure is explained by frustrating nn (diagonal) interactions. Apparently, the magnetic interactions in CaCrO$_3$ are governed by sizeable $pd$ hybridization, a generic consequence of the high oxidation state associated with a small or negative charge transfer gap.

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