CrO$_2$ is a canonical example of a half metallic ferromagnet (HMFM), exhibiting an experimental observation of nearly 100\% spin polarization of the charge carriers at the Fermi level\cite{1,2,3,4}. An interesting feature exhibited by this spintronic material is that electron transport is metallic in single crystal form whereas the granular samples show an \textit{activated behavior}. It is to be noted that the bulk magnetization in both cases shows no apparent difference. This unusual behavior is understood to be the outcome of strong grain boundary (GB) effects that governs the electronic conduction in this material\cite{3,4,5}. Here the inter grain conduction occurs through the (spin polarized) tunneling of charge carriers across insulating GB - a phenomenon which is central to the observation of enhanced magnetoresistance (MR) in granular CrO$_2$. \cite{6,7,8} The GB's that appear as a thin layer on the surface of the CrO$_2$ grain have been identified to be an antiferromagnetic (AFM) insulator Cr$_2$O$_3$. \cite{5,6,7} The typical thickness of the GB in commercially available CrO$_2$ powders is about 1-2 nm whereas the typical grain size is about 0.1-0.4 $\mu$m \cite{5,6}. The exact functional form of the conductance depends crucially on these microstructural parameters.

It is interesting to note that the transport mechanism as seen in CrO$_2$ as well as many such granular metals simply mimic the physical properties of tailor made conducting grains (with well defined shape and size) embedded in an insulator\cite{2,3,4,5}. For instance, commercial powders are seen to exhibit Coulomb Blockade (CB) effects at temperatures below 50 K \cite{3,4,5}, with the conductance exhibiting a characteristic $exp(-\Delta/T)^{1/2}$ dependence \cite{6,7}. Above 50 K, multi channel inelastic hopping through the localized states in the GB is seen to dominate the conductance. Overall, the functional form of conductance up to the room temperature can thus be written as \cite{2,3,4,5}

$$\sigma = B_1 exp(-\Delta/T)^{0.5} + C_1 T^{1.33} + C_2 T^{2.45} + ...$$ \hspace{1cm} (1)

$C_1, C_2$ are the higher order terms is the coefficient corresponding to the first and second order of hopping through the localized states of the GB. However, these hopping processes do not conserve spin and thus responsible for the rapid decline of spin polarization and consequently MR above 50 K in this spintronic material\cite{5,7}. This functional form of conductance is seen to be retained when GB thickness is increased by intentional dilution with Cr$_2$O$_3$. Though enhancing GB thickness improves the MR at low temperatures, it still decays rapidly above 50 K and is negligible near the room temperatures\cite{5,7}. Such studies also indicate that the electron transport and therefore MR in this material should be tuned by variation in crystallographic microstructure. Unfortunately, tuning these parameters without disturbing the HMFM phase of CrO$_2$ is a non trivial task, for it is a metastable phase with associated difficulties in synthesis \cite{11}. These factors severely limit the tunability factor of various microstructural parameters and most magnetotransport measurements on this material have been reported on commercially available powders, which were basically meant for magnetic recording industries.

In this letter, we report electrical transport measurements in pure as well as highly diluted samples of granular CrO$_2$ with substantially enhanced grain size, roughly an order of magnitude larger than what is seen in commercial powders. These samples were synthesized in cold pressed powders as well as sintered pellets form, while retaining the phase purity and characterized by X-ray diffraction (XRD) bulk magnetization and Scanning Electron Microscopy (SEM) etc. \cite{12,13}. The transport measurements were made using PPMS -9 (Quantum Design) by using the standard four probe technique in the temperature range of 5-320 K. Fig. 1 summarizes the characterization measurements on a pure and sintered CrO$_2$ sample, the details of which can be found elsewhere\cite{13}. It is to be noted that we categorize 'pure CrO$_2$' as samples in which saturation magnetization (Ms) falls between 125-135 emu/g\cite{14}. These samples do not
exhibit any visible peak corresponding to the insulating oxide Cr$_2$O$_3$ in XRD patterns. By suitable variation in synthesis condition, the mass fraction of Cr$_2$O$_3$ can be systematically increased, which is then visible in XRD and is quantified\cite{12}. We also present transport measurements on samples in which GB density was increased by Cr$_2$O$_5$, another AFM insulator having lower $T_X$ than Cr$_2$O$_3$. The transport measurement on these composites bring out the crucial role played by the AFM character of GB in magnetotransport in granular CrO$_2$, an aspect which is less adequately addressed in literature as far as bulk samples are concerned. Exploring this material with varying crystallographic microstructure enables the observation of a different functional form of activated transport which is evidently related with the significantly enhanced MR properties in these samples.

Fig.2 displays zero field conductance as a function of temperature for pure and diluted samples of CrO$_2$. The data set can be roughly divided into two temperature regions, the lower side of region I exhibits a practically linear temperature dependence, followed by a sudden rise in conductance occurs in region II (between 240-300 K), which was not seen in granular CrO$_2$ prior to this work. Though conductance follows an activated behavior in both the regions, as is expected in granular CrO$_2$, its temperature dependence could not be fitted with either the CB term or its combination with any other hopping terms as given in eq.1\cite{3,4} in the temperature range of measurement. It is to be noted that the CB energy has been calculated to be about 13 K\cite{4} for commercially available CrO$_2$ powders with about 0.1 $\mu$m grain size, whereas the grain size in our samples is 1-10 $\mu$m\cite{13}. Thus the absence of CB effects in the lower temperature region is not surprising due to the larger grain size\cite{10}. However, this data does not fit to any of the spin independent hopping described in eq.1 in higher temperature region as well, in which the conductance rises much sharply and with a opposite curvature than what is predicted by higher order terms of Eq.1.

We find that the functional form of conductance in region I is best described on the basis of a Fluctuation Induced Tunneling (FIT) model meant for conducting grains separated by insulating barriers\cite{12}. One essential ingredient of this model is that the conducting grains are large enough so as to overcome the Coulomb Blockade regime. The tunnel barrier is considered to be in the form of rectangular tunnel junction of area ’A’ and width ’w’. When such a tunnel junction is kept under a thermal bath, apart from the externally applied field $E_A$, there is an additional source of the field, which arises due to thermal fluctuations leading to a voltage difference across the junction. Most remarkably, it was seen that the underlying approximations, which are meant for a single tunnel junction can be used to describe a network of independently fluctuating tunnel junctions\cite{15} and the final form of conductance can be given by\cite{15}.

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T+T_0}\right)$$ \hspace{1cm} (2)

here $T_1 = uE_0^2/k_B$, $T_0 = 2uE_0^2/\pi\chi w k_B$, $E_0 = 4V_0/\pi w$, $u = wA/8\pi$, $\chi = (2mV_0/h^2)^{1/2}$ and $V_0$ is the height of the potential barrier\cite{12}.

The data set in Fig.2 fits well to Eq. 2 with single set of parameters roughly upto 200 K . The ratio $T_1/T_0$ directly gives an estimate for barrier thickness if $V_0$ is known. We estimate the parameter ’w’ for the pure CrO$_2$ by taking $V_0$ to be 0.7 eV\cite{10} for CrO$_2$. This yields ’w’ to be of the order of 2A which appears a feasible value for tunnel barrier thickness. Similar fits were obtained on pure samples prepared in different batches in both cold pressed as well as in sintered form. Though FIT is seen in granular CrO$_2$ samples for the first time, it is important to recall that is found to be most appropriate model for many other granular oxide samples which exhibit intergranular tunneling. These include double pervoskite Sr$_2$FeMoO$_6$\cite{17} and very recently Sr$_2$CrWO$_6$\cite{18}.

Dilution\cite{12,13} of CrO$_2$ with insulating oxide Cr$_2$O$_3$ or CrO$_3$ also follows a similar functional form as is observed for pure CrO$_2$ in lower temperature region.(Fig 2b). Though functional form of conductance follows FIT even in highly diluted samples irrespective of the type of insulator- some subtle differences appear in region I. For instance, when the quantity $(1/\rho)(d\rho/dT)$ is plotted as a function of temperature for pure CrO$_2$ and CrO$_2$/Cr$_2$O$_5$ composites, all the data practically collapse into a single curve roughly upto 200 K as is shown in the main panel of Fig.3. The CrO$_2$/ Cr$_2$O$_3$ composites do not follow this pattern as can be seen in the inset of Fig.3 where data on both composites is plotted together. This can be attributed to a strikingly different value of parameter $T_1$ as seen in Cr$_2$O$_3$ composites. Considering the functional form of resistivity following Eq. 2, the quantity $(1/\rho)(d\rho/dT)$ is given by $-T_1/(T+T_0)^2$. In the inset of Fig.3, the solid line is the function $-T_1/(T+T_0)^2$ for which $T_1$ and $T_0$ have been obtained from the fit of $\sigma$ vs $T$ data for each composite. This separates out the region in which FIT dominate in a clear fashion and brings out the robustness of the FIT conductance in pure and diluted CrO$_2$ samples. Most importantly, it also gives a clue about the role of the magnetic nature of GB on the functional form of zero field conductance. Though FIT model does not take care of magnetic interactions explicitly, its influence on the tunneling probability should reflect in the nature of the potential barrier, as it appears from the fitting parameters as obtained on samples with different type of GB.

The functional form of the conductance in region II where a sudden rise occurs could not be explained by FIT model alone. As is evident from Fig2, the sharpness of 240 K feature varies with the type of GB. We observe that enhancing the GB density by Cr$_2$O$_5$ reduces
the sharpness of the step in conductance, however in the presence of Cr$_2$O$_3$ the functional form of conductance is qualitatively similar to what is seen in pure CrO$_2$. It is to be noted that in the vicinity of the step, Cr$_2$O$_3$ is an AFM insulator whereas Cr$_2$O$_5$ is a paramagnetic insulator. Though it is difficult to separate out the contribution of grain or the GB from the present data, but it is clear from Fig. 2 that the magnetic state of GB does play a role. The sudden rise in conductance plays a crucial role in determining the evolution of MR as a function of temperature.

In conclusion we have demonstrated that by modulations in grain size, type and mass fraction of grain boundary density, we are able to observe a different functional form of activated transport in granular CrO$_2$. In a wide temperature range, this is best described by Fluctuation Induced Tunneling irrespective of type and mass fraction of insulator. These data convey that tuning the insulating properties of CrO$_2$ is inhibited due to the charging energy ($e^2/C \approx \Delta$) winning over the thermal energy ($k_BT$) for a grain of capacitance $C$. Consequently, the temperature range in which the Coulomb Blockade dominates is decided by the grain size.

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FIG. 1: Magnetization as a function of Temperature for pure and sintered CrO$_2$. Lower inset displays SEM picture exhibiting grains with average length of about 5 microns. Upper inset exhibits specific heat as a function of temperature for the same sample.

FIG. 2: (a) displays $\sigma$ Vs T for pure CrO$_2$. The data is consistent with the previous observation of activated behavior for granular CrO$_2$, but with a different functional form in the entire temperature range of measurement. The vertical line demarcate two distinct regions of activated transport. Solid lines in main panel is the fit of FIT model (eq.2) to the conductivity data. (b) displays the same for CrO$_2$/Cr$_2$O$_5$ (triangles) and CrO$_2$/Cr$_2$O$_3$ composites (stars). The mass fraction of CrO$_2$ in each of these composites is nearly 50%.

FIG. 3: The main panel shows the quantity $(1/\rho)(d\rho/dT)$ as a function of temperature, for pure CrO$_2$ and CrO$_2$/Cr$_2$O$_5$ composites with varying mass fraction of CrO$_2$. Inset shows the same plot for a CrO$_2$/Cr$_2$O$_3$ (stars) together with a CrO$_2$/Cr$_2$O$_5$ (triangles) composite. Solid lines in the inset are the function $[-T_1/(T+T_0)^2]$ plotted against temperature, where the corresponding values of T$_1$ and T$_0$ have been obtained from the $\sigma$ vs T curves for each sample.

FIG. 4: $\sigma$ Vs T measured at 0, 2 and 5 Tesla for a pure CrO$_2$. Solid lines in each data set are the fit of eq.2 to the data. The applied magnetic field does alters the parameters T$_1$ and T$_0$ though their ratio does not show variation. The deviation from FIT is also marked by the change in the temperature dependence of MR as is evident from the figure.
Fig. 1
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Fig. 2
A. Bajpai and A. K. Nigam

Pure CrO$_2$
$\sigma = 2.38\exp[-232/(T+181)]$

CrO$_2$/Cr$_2$O$_5$
$\sigma = 1.39\exp[-238/(T+181)]$

CrO$_2$/Cr$_2$O$_3$
$\sigma = 0.12\exp[-380/(T+180)]$
Fig. 3
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Fig. 4
A. Bajpai and A. K. Nigam