Non-linear electrical response in a charge/orbital ordered Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ crystal : the charge density wave analogy.

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Abstract

Non-linear conduction in a charge-ordered manganese oxide Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ is reported. To interpret such a feature, it is usually proposed that a breakdown of the charge or orbitally ordered state is induced by the current. The system behaves in such a way that the bias current may generate metallic paths giving rise to resistivity drop. One can describe this feature by considering the coexistence of localized and delocalized electron states with independent paths of conduction. This situation is reminiscent of what occurs in charge density wave systems where a similar non-linear conduction is also observed. In the light of recent experimental results suggesting the development of charge density waves in charge and orbitally ordered manganese oxides, a phenomenological model for charge density waves motion is used to describe the non-linear conduction in Pr$_{0.63}$Ca$_{0.37}$MnO$_3$. In such a framework, the non-linear conduction arises from the motion of the charge density waves condensate which carries
a net electrical current.
Charge ordering (CO) is a common characteristic of transition metal oxides with perovskite structure.\textsuperscript{1} In colossal magnetoresistive (CMR) manganites, the formation of an $Mn^{3+} : Mn^{4+}$ ordered phase is the most obvious manifestation of the $e_g$ electrons localization.\textsuperscript{2,3} The physics of the phase transition from a CO - antiferromagnet to charge-delocalized ferromagnet have been extensively studied in recent years. This CO destabilization is of great interest because this feature can be achieved under a wide variety of external perturbations.\textsuperscript{4–9} For instance, numerous experimental results have shown that the application of a moderate electric field leads to an insulator - metal (I-M) transition associated with a strong non-linearity of the voltage - current (V-I) characteristics.\textsuperscript{10–15} To interpret such a phenomenon it is proposed that a breakdown of the CO state is induced by the current and that metallic filaments are created. However, when considering the properties of manganites with colossal magnetoresistance, one have also to take into account, besides the charge and spin degrees of freedom, the orbital structure of the transition metal ions. Therefore, the description of the collective behavior of $e_g$ carriers in connection with the specific kind of charge \textit{and} orbital ordering (OO) (which depend on the doping state) might be of fundamental interest for the understanding of the non-linear electrical response of the CO / OO manganites.\textsuperscript{10–15}

Compounds of the system $Pr_{1-x}Ca_xMnO_3$ with $x$ close to 0.4 is a well documented material for which extensive investigations have been carried out by magnetic and transport measurements.\textsuperscript{4,5,16–20} Recently, in $Pr_{0.63}Ca_{0.37}MnO_3$,Asaka et al.\textsuperscript{21}, by means of low-temperature electron microscopy have revealed new forms of structural modulations that are discussed in terms of temperature-dependent ordering of $e_g$ electrons. These authors have observed superlattice reflection spots with a modulation wave vector $q_1 = (0,\frac{1}{2},0)$ below 230 K, suggesting the classical formation of $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbital ordering, similar to the half-doped manganite $Pr_{0.5}Ca_{0.5}MnO_3$. Below 150 K, a new modulation wave vector appears, $q_2 = (\frac{1}{7},\frac{1}{7},\frac{1}{7})$. In this temperature range, $Mn^{3+}$ ions must be substituted partially on the $Mn^{4+}$ sublattice in the $x = \frac{1}{2}$ type CO / OO in the ratio 1:3. This kind of ordering can be viewed as a quasi-one dimensional electronic structure with a reduced dimensionality.
compared to the 1:1 CO / OO of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. This low temperature electronic structure is described as follows along the $c-axis$: a $d_{3z^2-r^2}$/$d_{3y^2-r^2}$ orbital ordering of $Mn^{3+}$ occurs while in an adjacent plane, the $d_{3z^2-r^2}$ orbitals of the $Mn^{3+}$ are separated by three $Mn^{4+}$ ions. Such a periodic arrangement (non commensurate) of charge in Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ might lead to the development of a charge density wave (CDW) condensate. Such a CDW formation has also been deduced recently in manganese oxides of this composition by means of angle resolved photoemission spectroscopy.$^{22}$ By means of THz time-domain spectroscopy,$^{23}$ evidence for a charge density wave condensate in the CO / OO manganite Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ has been reported. For this composition, Kida et al.$^{23}$ have revealed the existence of a finite peak structure well below the charge gap. They attributed this observed structure to the collective excitation mode arising from a charge density wave condensate.

The more fascinating properties of CDW systems are related to nonlinear conduction induced by an electric field.$^{24}$ This feature was interpreted as the conductivity associated with the motion of CDW. As proposed in$^{25}$, the phase of the CDW could be pinned by several mechanisms; if an electric field strong enough to overcome the pinning energy were applied, the CDW can be depinned and carries a current. In the following, on the basis of the experimental observations suggesting a CDW development in manganese oxides$^{23,22,26}$, we tentatively account for non-linear V-I characteristics in Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ by considering a phenomenological model for CDW motion.$^{27}$

Using the floating-zone method with a feeding rod of nominal composition Pr$_{0.6}$Ca$_{0.4}$MnO$_3$, a several-cm-long single crystal was grown in a mirror furnace. X-ray diffraction and electron diffraction studies, which were performed on pieces coming from the same part of the crystal, attested that the samples are single phased, and well crystallized. The cell is orthorhombic with a Pnma space group, in agreement with previously reported structural data. The electron diffraction (ED) investigations have shown the existence of twinning domains, which result from the reversible phase transitions (from cubic to orthorhombic) undergone by the crystals upon cooling. The cationic composition derived from energy-dispersive x-ray analyses leads to the formula Pr$_{0.63}$Ca$_{0.37}$MnO$_3$. Four linear
contact pads of In were soldered onto the sample in linear four-probe configuration. $V-I$ data were taken with current biasing (Keithley 236) and with a temperature control of 100 mK.

In figure 1, the temperature variation of the resistivity ($\rho \text{ vs } T$) of a $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$ crystal is shown for various bias current under zero magnetic field. For low current, the $\rho \text{ vs } T$ curve displays a pronounced semiconducting-like behavior, leading to an insulating state at low temperatures. Our current source overloads for $V_{\text{lim}} = 100\text{V}$, thus the maximum measurable resistance for $10^{-3}\text{mA}$ is around $100\text{M}\Omega$. For higher current, the insulating state is no longer observable; the resistivity is indeed strongly depressed. There is no true insulator - metal transition but a trend to saturation when the temperature is lowered. Moreover, for high and low currents, one can also denote a clear kink around 230K, which related to the charge ordering phenomenon. Figure 2 shows V-I characteristics for various temperatures (60K, 80K, 120K and 140K). A strong non-linearity i.e. a deviation from the Ohm’s law, is observed when the bias current attains a threshold value (0.66 A.cm$^{-2}$ at 80K). This non-linearity is even more obvious when $\frac{R}{R_{\text{ohmic}}} \text{ vs } I$ curves are plotted (See figure 3). As expected the resistance is independent of the bias current in the ohmic regime and is strongly decreased for a critical value of the current. One can observe that the current value where the non-linearity sets in and the width of the transition are strongly temperature dependent (both increase as the temperature increases). Because of the rounding of the variation of $\frac{R}{R_{\text{ohmic}}} \text{ vs } I$, it is very difficult to define a value for a critical current.

We have carefully checked that the Joule heating is irrelevant to account for this current induced effect. The temperature rise of the sample with respect to the sample holder ($\Delta T$) has been measured by attaching a thermometer on the top of the sample itself. In the low temperature range and for the highest power dissipation, one measure $\Delta T \prec 6\text{K}$. For higher temperature of measurements, $\Delta T$ becomes negligible. Moreover, a great amount of papers have verified this point in samples of the same composition. The peculiar electrical response that we describe here is in remarkable agreement with previous studies carried out on CO / OO manganese oxides.$^{10-15}$ To account for the nonlinear conduction in CO / OO
manganese oxides, a special type of dielectric breakdown of the CO state brought about by small electric field is invoked. It is argued that the barrier between the CO state and the metallic state is small enough that a small electric field can cause an I-M transition.\textsuperscript{10–15} The system behaves in such a way that the bias current may generate metallic path giving rise to resistivity drop. One can describe this feature by considering coexistence of localized and delocalized electron states with independent path of conduction. This situation is analogous to what occurs in charge density waves systems.\textsuperscript{24}

In the following, we propose that, for Pr\textsubscript{0.63}Ca\textsubscript{0.37}MnO\textsubscript{3}, the non-linearity observed in V-I characteristics can be linked to the collective excitation of the CDW condensate. By analogy with the sliding mode conductivity in NbSe\textsubscript{3},\textsuperscript{24,27} the non-linear transport properties are explained by the motion of charge density waves, which carry a net electrical current, superimposed to the poorly mobile carriers of the system, when the current reaches a critical current necessary to overcome the pinning forces acting on the CDW condensate. The total current density can then be written: \( j = j_{CDW} + \sigma E \) where \( j_{CDW} \) is the current density associated with the motion of the CDW condensate and \( \sigma \) is the ohmic conductivity at low electric field / current. The dynamic of the collective mode is described in terms of a position- and time-dependent order parameter, thus both amplitude and phase fluctuation occur. The relevant collective mode is the phase one which is gapless. As described by Grüner et al.\textsuperscript{24}, the phase mode carries a dipole moment as it corresponds to the motion of condensed electrons through the background of position changes of the ions; consequently, the phase mode carries a current for a wave vector \( q = 0 \). Monceau et al.\textsuperscript{27} have developed a model where the phase of the CDW is described as an overdamped oscillator. The non-linear electrical response is the consequence of the interaction between the phase mode and the lattice. These interactions lead to a finite pinning energy and consequently to a finite bias current for the non-linear conduction to set in. In the manganese oxides of the system Pr\textsubscript{1–x}Ca\textsubscript{x}MnO\textsubscript{3}, the pinning centers that we are dealing with are not well identified. The pinning is expected on general grounds, e. g. the L/A substitutional disorder that acts as a quenched disorder, other lattice defects or possible homogeneities. To be more precise,
in these materials, the Jahn-Teller ions Mn3+ has a major role. The Jahn-Teller induced distortion of the Mn3+O6 octahedra can act as a periodic pinning site due to local strain field. Very early in the subject\textsuperscript{28}, these strain fields have been observed by high resolution electron microscopy in Pr manganites. Existence of monoclinic domains in the orthorhombic matrix corresponding to a modification of the geometry of the Mn\textsuperscript{3+}O\textsubscript{6} octahedra has been reported. At the junction between the two kinds of domains, a defective structure is observed and can be interpreted as a twin boundary. In the Pr manganites, another very important feature deals with the existence of a rather large density of isolated point defects. Once again, this can be associated with the local modification of the manganese environment owing to the Jahn-Teller effect.

Neglecting inertial effects and considering the phase $\phi(r,t)$ as uniform throughout a given domain, the equation of motion of the phase obtained in the framework of the ”single particle” model is:

$$\tau \frac{\partial \phi}{\partial t} (1 + \beta) = \frac{j}{\sigma E_c} + \sin \phi$$

where $\phi$ is the phase of the domain, $\beta$ is an experimental parameter defined as $\beta = \frac{\sigma_{E \to \infty} - \sigma_{E \to 0}}{\sigma_{E \to 0}}$, $\tau$ is a dimensionless parameter. When the applied current is constant the average electric field is:

$$E = \frac{j}{\sigma} - \frac{\beta E_c}{1 + \beta} \left[ \left( \frac{j}{j_c} \right)^2 - 1 \right]^{\frac{1}{2}}$$

where $\sigma$ is the ohmic conductivity, $E_c$ and $j_c$ are the critical electric field and current, respectively, where the non-linearity sets in. Introducing the experimental variables $R$, the measured resistance and $I$, the applied current, one obtains:

$$R = R_{ohmic} \left[ 1 - \left( \frac{\beta}{1 + \beta} \right) \left[ 1 - \frac{I_c^2}{I^2} \right]^{\frac{1}{2}} \right]$$

According to Monceau et al.\textsuperscript{27}, to account for a more realistic description of the sample, we assume that it is formed of multiple domains. A statistical distribution of domains is then considered, each one being depinned for a given value of $I_c$, in a mean field approximation.
Let us call $P(I_c) dI_c$, the normalized probability to observe the depinning of a domain for a current value in the range $I_c + dI_c$ and $I_c$. $m$ is the mean value of this statistical distribution and $s$, the standard deviation. The resistance of the system is then given by:

$$R = R_{\text{ohmic}} \left[ 1 - \left( \frac{\beta}{1+\beta} \right) \int_{I_{\text{Ohmic}}}^{I_c} P(I_c) \left[ 1 - \frac{I_c^2}{I_{\text{Ohmic}}^2} \right]^{\frac{1}{2}} dI_c \right]$$

$I_{\text{Ohmic}}$ is a cutoff corresponding to the current for which the first domain is depinned. The range $I < I_{\text{Ohmic}}$ defines the true ohmic response.

This model is essentially phenomenological. The main assumption of the mean field approach is to assume a statistical distribution for critical currents. Originally, Monceau et al.\textsuperscript{27} have used a gaussian distribution without any justification. According to the literature, the properties of the CDW systems are very similar to the typical properties of the wide range of glass materials. The description of the behaviour of many glass materials often uses the hypothesis about dynamic scaling. On this base, the dynamic effects in disordered glass material have been considered.\textsuperscript{29–32} In particular, it was shown that in correlated systems with some disorder, the lognormal distribution for relaxation times is relevant.\textsuperscript{29–32}

The expression of the distribution we have used is:

$$P(I_c) = \frac{1}{I_c \beta \sqrt{2\pi}} \exp \left[ -\frac{(\ln I_c - \ln \alpha)^2}{2\beta^2} \right]$$

with $\alpha = m \sqrt{k}$, $\beta = \ln k$ and $k = \left( \frac{\alpha}{m} \right)^2 + 1$. $m$ and $s$ are the mean and the standard deviation respectively.

The results are shown in figure 4 for $T = 80K$. One observe a good agreement between the predicted model (solid lines) and the experimental $R$ vs $I$ curves (symbols). The same agreement is found for other temperatures. Figure 4 can not be considered as experimental evidence by itself. Nevertheless, in the first part of the paper, we discuss the experimental evidences for the occurrence of a charge density wave in the CO manganites. Within this framework, the issue is then to test if a model, which has been successfully applied for archetypal CDW systems, can describe our data. Thus, figure 4 suggests that an analogy between the CDW domains sliding and the non-linear conduction in CO manganites might be
reliable. In figure 5, the distributions calculated from the fit parameters are shown for various temperatures. In addition, the temperature dependence of the standard deviation ($s$) and mean ($m$) are reported in figure 6. Those two parameters are of great interest since their temperature dependence can be understood in light of our knowledge concerning the stability of the CO / OO state in Pr$_{0.63}$Ca$_{0.37}$MnO$_3$.\textsuperscript{21} The temperature dependence of $s$ (main panel figure 6) gives a good picture of the homogeneity of the CO / OO state (that is at the origin of the development of the CDW condensate). From low temperature up to 100 K, there is only a slight variation of $s$ with the temperature while above this temperature, the value of $s$ is substantially increased. This feature can be related with the two modulation structure observed by Asaka et al.\textsuperscript{21} Below 230 K, a CO / OO state of the $d_{3x^2−r^2}/d_{3y^2−r^2}$ orbitals of the Mn$^{3+}$ similar to the half-doped Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ remains essential ((CO / OO)$_q$). While the temperature is decreased, a new modulation structure corresponding to a partial substitution of Mn$^{3+}$ on the Mn$^{4+}$ sublattice in ratio 1:3 appears ((CO / OO)$_{q_2}$). The (CO / OO)$_{q_2}$, which is long range for $T = 100K$, modifies the uniformity of the charge density, leading to the development of a CDW condensate. Our $s$ vs $T$ data can be understood on the basis of this observation. At low temperature, the (CO / OO)$_{q_2}$ state is rather homogenous and long range, leading to a small width of the statistical distribution of $I_c$ since there is not a great variety of domains that have to be depinned. As the temperature increases, the (CO / OO)$_{q_2}$ is no longer long range and a fragmentation of the CDW lattice into smaller domains occurs. Consequently, one observes an increase of the width of the distribution. The temperature dependence of the mean is less easy to understand (inset figure 6). It appears that the current necessary to depin a domain increases with temperature. Arguing from analogy with the NbSe$_3$ system, this feature might be related to the size of the (CO / OO)$_{q_2}$ domains where the CDW is developed. In the model proposed by Monceau et al.\textsuperscript{27}, the interactions between pinning centers and the phase of the CDW can be written:

$$W_{\text{interact}} = -V_0 \cos[\phi(r_i) - \psi(r_i)]$$

where $r_i$ is the position of a pinning center, $\phi$, the phase of the CDW and $\psi$, the ideal value of the phase for an effective pinning. Below 230 K, there is a nucleation of small (CO / OO)$_{q_2}$ CDW domains at places where the random distribution
of pinning centers (i.e. of $\psi(r_i)$ values) fixes the phase of the domain in an attractive position corresponding to higher depinning current. As the temperature decreases down to 100 K, the domains are growing, encompassing less favorable value of $\psi$ and consequently, lower currents are necessary to depin them.

In conclusion, V-I characteristics have been measured in a Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ crystal. Strong non-linear conduction is observed under zero field for a wide range of temperature. This feature is reminiscent of what is observed in charge density waves systems. On the basis of the experimental observations suggesting a CDW development in manganese oxides, we speculate that non-linear conduction in Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ can be described by considering a phenomenological model for CDW motion.
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I. FIGURES CAPTIONS

**Figure 1**: Temperature dependence of resistance for a Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ crystal with various bias currents.

**Figure 2**: $V-I$ characteristics under zero field for various temperatures (60K, 80K, 120K and 140K).

**Figure 3**: $\frac{R}{R_{Ohmic}}$ versus bias current for various temperatures.

**Figure 4**: $R$ versus bias current at 80K. The solid line is the fit using the model described in the text.

**Figure 5**: Shape of the distributions of $I_c$ for various temperatures.

**Figure 6**: Temperature dependence of the standard deviation (s) of the distribution. Inset: Temperature dependence of the mean (m) of the distribution.