# Photo-Induced Magnetism in La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> with Canted Antiferromagnetic Spin Order Studied by Electron Spin Resonance.

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Photo-magnetic properties on the distorted perovskite chromates,  $La_{0.5}Pr_{0.5}CrO_3$  (Space group : *Pnma* at 300 K) was studied by X-band (9.0 GHz) Electron Spin Resonance (ESR). The  $La_{0.5}Pr_{0.5}CrO_3$  shows the canted antiferromagnetic (CAF) transition at  $T_{CAF} \sim 261$  K and the magnetic domains with random orientation of ferromagnetic component in the CAF spin order below the  $T_{CAF}$ . A YAG laser with photon energy  $h_0 = 1.17$  eV (wavelength  $\lambda = 10640$  Å) which is near infrared region was employed for a photo injection. During the photo injection, the ESR intensity increases dramatically around the  $T_{CAF}$ . The observed photo-induced ESR profiles retain Lorentzian curvature with center resonance magnetic field, 320 mT. The photo-induced ESR intensity increase gradually with a increase in temperature up to the  $T_{CAF}$  i.e. the CAF state and grow up dramatically above the  $T_{CAF}$  i.e. the paramagnetic state. This high  $T_{CAF}$  allows us to provide photo-magnetic functional devices operated at room temperature. This transient magnetization was with the characteristic thermal activation energy of 130 meV. The present results open an intriguing possibility of collective photo-induced magnetism in the distorted perovskite chromates.

Keywords : Magnetic materials., Chromates., Photo-induced effect., Electron paramagnetic resonance., Near-infrared light.

# 1. INTRODUCTION

To meet a recent industrial demand such as photo-magnetic hybrid device, with which one can control the electric property by the photo injection and/ or the magnetic field, photo-induced phenomena are intensively studied. The photo-induced phenomena also has been attracted great academic interests as a frontier for post superconductivity in the strongly correlate system. There are tow types of approach to the photo-induced phenomena. One is compound mixed with ferromagnet and ferrimagnet<sup>[1]</sup> and other is with the canted antiferromagnetic (CAF) spin order. Both type of compounds have mach frustration in spin system and are easily achieved phase transition by various external stimulation such as light, magnetic field, electric field, pressure and etc.

In Prussian blue analog with mixed ferromagnet and ferrimagnet, photo-induced effects have been

reported  $^{[2,3]}$ . The Prussian blue are molecular magnets with a relative high Curie temperature. For  $(M_x^{2+}Mn_{1+x}^{2+})_{1.5}Cr^{3+}(CN)_6~(M=Ni^{2+}~or~Fe^{2+})$ , depending on the mixing rate x, the magnetic pole can be inverted by the light illumination. This is Optimized tuning ferromagnetic and ferrimagnetic exchange interactions induced by the light illumination.

In the distorted perovskite manganese,  $La_{1-x}Sr_x$ MnO<sub>3-d</sub>, there are tow types of photo-induced effects. One is persistent photoconductivity and other is transient one<sup>[4]</sup>.  $La_{1-x}Sr_xMnO_{3-d}$  (0.2  $\leq x \leq$  0.5) with mixed Mn<sup>3+</sup> and Mn<sup>4+</sup> shows ferromagnetic metal transition and so-call colossal magnetoresistance (CMR) around this transition temperature. At small oxygen deficiency, it shows metallic behavior in dark and is induced persistent photoconductivity under a white light illumination. On the country, at large oxygen deficiency, the film is semiconductor in dark and the transient photoconductivity is induced by the light

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illumination.

Recent progress on the survey of photo-induced effect in  $Pr_{0.65}Ca_{0.35}MnO_3^{[5, 6]}$  is reported with respect to the electron spin resonance (ESR)<sup>[7, 8]</sup> and the powder x -ray diffraction<sup>[9, 10]</sup>. This photo-induced effect is reported in the charge-ordered (CO) state formed by the alternation of Mn<sup>3+</sup> and Mn<sup>4+</sup> ions associated with the CAF spin order. First, the paramagnetic resonance, which is diminished at the onset of the CAF spin order, revives under the photo injection by nearinfrared cw-YAG laser with a photon energy, hv =1.17 eV. Second, the superlattice reflections, which are from the CO structure not suppressed by only Xray irradiated for the diffraction study, are suppressed under the photo injection, leading to the structural evidence of the collapse of the CO state by the photo injection. The present results indicate that the photoinduced paramagnetic resonance is associated with the melting of the CO structure.

In this communication, we focus on chromates, La<sub>0.5</sub> Pr<sub>0.5</sub>CrO<sub>3</sub> as a new candidate for the photo-magnetic material from the distorted perovskite type transition metal oxide. The  $Cr^{3+}$  (3d<sup>3</sup>) in La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> is very similar to  $Mn^{4+}$  (3d<sup>3</sup>) in the manganese,  $Pr_{0.65}Ca_{0.35}$ MnO<sub>3</sub> where either spin is S = 3/2 in the  $t_{2g}$  state. The La\_{0.5}Pr\_{0.5}CrO\_3 shows the CAF transition at  $T_{CAF}$  ~ 261 K and the magnetic domains with random orientation of ferromagnetic component in the CAF spin order below the  $T_{CAF}$  <sup>[11, 12]</sup>. This high  $T_{CAF}$  may allows us to provide photo-magnetic functional devices operated at room temperature. The magnetic domain is easily suppressed by the external stimulation. The photo-induced effect in La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> was investigated by the X-band (9.0 GHz) ESR under the photo injection with unique photon energy hv = 1.17 eV (wavelength  $\lambda$  = 10640 Å) which is near infrared region.

# 2. EXPERIMENT

The powder samples of La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> were carefully prepared by calcining the mixture of prescribed amount of Pr<sub>6</sub>O<sub>11</sub> (99.9%), Cr<sub>2</sub>O<sub>3</sub> (99.98%) and La<sub>2</sub>O<sub>3</sub> (99.99%). The mixed powder was made into a pellet and precalcined in air atmosphere at 1100 for 24 h. Then the pellet was ground, made into a pellet again and calcined in oxygen atmosphere at 1350 for 24 h<sup>[11, 12, 13]</sup>.

The powder x-ray diffraction measurement was carried out to verify the existence of single  $La_{0.5}Pr_{0.5}$ 

CrO<sub>3</sub> phase and to obtain the lattice constants. In the powder x-ray diffraction measurement, powder samples were attached to copper sample holder. Data were collected using powder diffractometer (Rigaku, RAD-IIB) with Cu *Ka* radiation ( $\lambda = 1.5418$  Å) equipped with a rotating anode generator operated at 40 kV and 200 mA. The 2  $\theta$  -  $\theta$  step scan was used with step width  $\Delta \theta = 0.01 - 0.02$  °, accumulation time 10 - 100 s/step. The calculation of the observed structure factor together with both profile fitting process and the refinement of crystal structure based on the powder x-ray diffraction data was performed by Rietveld method with a program RIETAN<sup>[14]</sup>.

D.c. magnetization was measured by SQUID magnetometer (Quantum Design, 7T-MPMS) to obtain complementary magnetic information. The d.c. magnetization was measured under the magnetic field 0.01 T under the sequence in the field cooling run (FC) and the zero field cooling run (ZFC). In the ZFC measurements were performed after sample was cooled down to a prescribed temperature under zero magnetic field, then a magnetic field was raised to 0.01 T. Magnetization vs magnetic field (M-H) curve was measured in the ZFC with magnetic field up to 7 T at 5 K.

The ESR measurement for the electron spin on  $Cr^{3+}$  ionic sites in  $La_{0.5}Pr_{0.5}CrO_3$  was done using the Xband spectrometer (JEOL, JES-RE1X) operated at 9.0 GHz with a 100 kHz field modulation. The resonance absorption of the ESR measurement was observed as a derivative signal curve. The sample was mounted in a liq. He continuous-flow type cryostat and was cooled from 300 K down to 10 K. The sample temperature was monitored by thermometer located near sample and was controlled by varying the flow rate of liq. He.  $Mn^{2+}$  diluted in MgO was employed for a reference.

To investigate a photo-induced effect, a cw Nd-YAG laser with unique photon energy hv = 1.17 eV were employed for the photo injection. The laser light was introduced into the sample situated in a cavity resonator through a double shielded quartz tubes belonging to the continuous flow He cryostat. The laser power was adjusted with the Kapton films which were 5 mW (4 sheets), 93 mW (3 sheets), 107 mW (2 sheets), 120 mW (1 sheet) and 175 mW (without sheet). The laser power of 175 mW is equivalent to the injection of  $9 \times 10^{17}$  photons/sec. It is noted that the described value of the monitored laser power does not indicate the precise value injected into the samples due to the existence of the tow quartz tubes as mentioned above. The laser spot size was about 1 mm<sup>2</sup>. The penetration depth of the laser light is estimated to be about 0.2 mm for the present sample. The ESR measurement was done under the sequence in which we measure the ESR profile without the photo injection, then under the photo injection and finally without the photo injection again in turn to check if any kinds of damage to the sample occur.

# 3. RESULTS AND DISCUSSION

Figure 1 shows the x-ray powder diffraction profile for La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> at 290 K with dot marks and the result of the profile fit by Rietveld analysis with solid lines. The x-ray powder diffraction analysis indicated that the present powder sample was in single phase with the distorted perovskite structure and symmetry is orthorhombic with the space group *Pnma* with lattice constants a = 5.475 Å, b = 7.741Å and c = 5.480 Å, respectively at 290 K.

Figure 2 shows the d.c. magnetization as a function of temperature in  $La_{0.5}Pr_{0.5}CrO_3$  under magnetic field 0.01 T in the FC and ZFC run with and

marks. The magnetization indicates a magnetic transition at  $T_{CAF} \sim 261$  K. A irreversible hysteresis between the FC and ZFC appears at the  $T_{CAF}$  and develops with decreasing temperature. This transition is attributed to the CAF transition. The magnetization in the FC is accompanied by a hump at 240 K. It decreases remarkably with decreasing temperature below 240 K. It passes through a magnetization value, M = 0 at 200 K, and sin of magnetization change from positive to negative in which is magnetization change from positive to negative in which is magnetization change up to minimum value = -250 emu/mol at 5 K. On the contrary, the magnetization in the FC remains at positive and its absolute value is relatively small.

In the La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub>, since La and Pr are trivalent rare earth element, all of Cr ions are Cr<sup>3+</sup>. The Cr 3*d* levels are separated by the oxygen octahedral crystal field to a lower energy  $t_{2g}$  orbital (triplet) and a higher energy  $e_g$  orbital (doublet). The Cr<sup>3+</sup> ion in the La<sub>0.5</sub> Pr<sub>0.5</sub>CrO<sub>3</sub> has a 3*d*<sup>3</sup> electron spin configuration  $t_{2g}^3$ . Hund's rule makes all spins align with each other on the atomic site by a large intra-atomic exchange. The  $t_{2g}$  orbital hybridize with O<sub>2p</sub> orbital much more weakly than the  $e_g$  orbital, and is regarded as forming the localized spin (*S* = 3/2). On the contrary, the  $e_g$ orbital have lobes directed to the counter oxygen atoms and hybridize strongly with O<sub>2p</sub> orbital, leading to the creation of rather broad bands.

In the antiferromagnetic spin order, each spins are arranged antiparallel like spin up, spin down, spin up due to the large antiferromagnetic exchange interaction. If there is frustration in the system, the spins arranged antiparallel are canted from antiparallel position. This is so-called CAF spin order. In the



Figure 1 The x-ray powder diffraction profile for  $La_{0.5}$  $Pr_{0.5}CrO_3$  at 290 K with dot marks and the result of the profile fit by Rietveld analysis with solid lines.



Figure 2 The d.c. magnetization as a function of temperature in  $La_{0.5}Pr_{0.5}CrO_3$  under magnetic field 0.01 T in the field cooling run (FC) and the zero field cooling run (ZFC) with and marks.



Figure 3 The ESR profiles for the La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> with and without (under dark) the photon injection by Nd-YAG laser ( $h\nu$  = 1.17 eV) with solid curves and broken curves.

CAF, there are relatively small ferromagnetic components. The present observation is a typical magnetic behavior in case of the existence of the spin-glass state. It attributes to the magnetic domains with random orientation of ferromagnetic component in the CAF spin order.

Figure 3 shows the ESR profiles for  $La_{0.5}Pr_{0.5}CrO_3$  without the photon injection (dark) as broken curves. Several sharp dips between 300 mT and 330 mT in the ESR profiles are coming from the  $Mn^{2+}$  as a reference. No ESR signal was observed from room temperature down to 10 K.

Figure 3 shows the ESR profiles for  $La_{0.5}Pr_{0.5}CrO_3$ with the photon injection ( $h\nu$  = 1.17 eV) as solid curves. No photo-induced ESR was observed below 210 K. During the photo injection, the ESR intensity increase dramatically around the  $T_{CAF}$ . The observed photo-induced ESR profiles retain Lorentzian curvature with center resonance magnetic field = 320 mT. The photo-induced ESR intensity increase gradually with a increase in temperature up to  $T_{CAF}$  i.e. the CAF state and grow up dramatically above  $T_{CAF}$  i.e. the paramagnetic state. The penetration depth of the laser light has been estimated to be about 0.2 µm for the present sample.



Figure 4 The ESR profiles for end compound of  $La_{1-x}Pr_xCrO_3$ , (0 < x < 1),  $LaCrO_3$  (a) and  $PrCrO_3$  (b) with and without the photon injection ( $h_D$  = 1.17 eV) with solid curves and broken curves at 290 K.

One might suspect that this transition is simply driven by the laser heating. The evidence against the laser heating is provided by the temperature dependence of ESR profiles. There is no difference among those profiles at low temperature where is expected to be sensitive for this kind of heating. This transition was reproducible, not permanent and also not due to any damage to the sample by laser irradiation. In fact, the ESR profile after the post-measurement with the photo injection shows almost identical with that obtained prior the measurement under the photo injection.

Figure 4 shows the ESR profiles for end compound of  $La_{1-x}Pr_xCrO_3$ , (0 < x < 1),  $LaCrO_3$  (a) and  $PrCrO_3$  (b) with and without the photon injection ( $h_{\mathcal{V}} = 1.17 \text{ eV}$ ) as solid curves and broken curves at 290 K. No remarkable change were observed in these ESR profiles with the photon injection. The observed photo -induced ESR intensity in  $La_{0.5}Pr_{0.5}CrO_3$  is attributed to arise from the solid solution of  $La_{1-x}Pr_xCrO_3$ .

Figure 5 shows temperature dependence of the photo-induced ESR intensity for La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> with the photon injection ( $h\nu$  = 1.17 eV). Below the T<sub>CAF</sub> ~ 261 K, it decrease with decreasing temperature and



Figure 5 Temperature dependence of the photoinduced ESR intensity for  $La_{0.5}Pr_{0.5}CrO_3$ with the photon injection ( $h\nu = 1.17$  eV).





Figure 6 The ESR profiles for various incident laser power (a) and incident laser power dependence of the photo-induced ESR intensity for  $La_{0.5}Pr_{0.5}CrO_3$  with the photon injection ( $h\nu$  = 1.17 eV) at 290 K.

follows the thermal activation type with characteristic energy of 130 meV. Above  $T_{CAF}$ , it is enhanced dramatically and deviating from the thermal activation type.

Figure 6 shows the ESR profiles for various incident laser power (a) and incident laser power dependence of the photo-induced ESR intensity for La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> with the photon injection ( $h\nu$  = 1.17 eV) at 290 K. There is obvious change in the ESR profiles and the effective spin susceptibility increases with a increasing the incident laser power. It is noted that the described value of the laser power does not mean the exact value injected to the samples due to the double shielded He flow guide made from quartz glass as mentioned above.

Time dependence of the photo-induced ESR intensity under the sequence of before, during and after the photon injection was also measured. It is worth to note that the relaxation of photo-induced ESR intensity is quite rapid.

The precise mechanism of the photo-induced magnetism in La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> is not clear in this present stage. However it may be important that the  $Cr^{3+}$  (3)  $d^{3}$ ) in La<sub>0.5</sub>Pr<sub>0.5</sub>CrO<sub>3</sub> is very similar to the Mn<sup>4+</sup> (3 $d^{3}$ ) in manganese,  $Pr_{0.65}Ca_{0.35}MnO_3$  where either spin is S =3/2 in the  $t_{2g}$  state. The photo-induced effect in Pr<sub>0.65</sub> Ca<sub>0.35</sub>MnO<sub>3</sub> is caused by the photo injection only with photon energy  $\sim 1.2$  eV which is near-infrared region. This energy value is characteristic in the optical spectra in these manganese. For example, there is a broad peak in the photoconductivity function centered around 1.2 eV in similar compound, La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub><sup>[6]</sup> and Nd<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub><sup>[15]</sup>. It is assigned as a chargetransfer excitation of an electron from the lower Jahn-Teller split  $e_g$  of Mn<sup>3+</sup> to the  $e_g$  of adjacent Mn<sup>4+</sup> ion, which exhibits the promotion of the dipole active photoionization of the Jahn-Teller small polaron<sup>[6]</sup>. Our present result suggests that the photon injection enhances the vibronic state and eventually releases the cooperative Jahn-Teller distortion associated with the CO state. The  $Mn^{3+}$  and  $Mn^{4+}$  in  $Pr_{0.65}Ca_{0.35}MnO_3$ have spin 3*d* electron configuration  $t_{2g}^3 e_g^1$  and  $t_{2g}^3$ . respectively. The possible optical charge transitions are from the spin up  $e_g$  levels in the Mn<sup>3+</sup> to the spin up  $e_g$  level of Mn<sup>4+</sup>. The spin up  $e_g$  levels in the Mn<sup>3+</sup> ions are split by  $E_{\rm JT}$  due to the Jahn-Teller effect. In the  $Mn^{4+}$  the spin up  $e_g$  states are shifted upwards (relative to the unsplit  $Mn^{3+}$  ion spin up  $e_g$  levels) by  $E_{\text{B}}$  due to the oxygen breathing mode distortions. The spin down  $e_g$  level of Mn<sup>4+</sup> is higher by Hund's coupling energy  $E_J = J_{H}S_c$  relative to the spin up  $e_g$  level of  $Mn^{4+}$ , where  $J_H$  is the exchange constant of Hund's coupling,  $S_c$  is the Mn ion core spin ( $S_c = 3/2$ ). The charge transition energy from the spin up  $e_g$  levels in the Mn<sup>3+</sup> to the spin up  $e_g$  level of Mn<sup>4+</sup> is about 1.2 eV<sup>[9]</sup>.

This process leads in promoting the hopping of an electron from a  $\text{Mn}^{\scriptscriptstyle 3^+}$  to a neighboring  $\text{Mn}^{\scriptscriptstyle 4^+}$  with the transfer energy, t and mixing species of Mn<sup>3+</sup> and Mn<sup>4+</sup> ion site. It corresponds to the transition from the CO state to the CD state with the metallic property. In other word, it is the photoionization of the Jahn-Teller small polaron. The large  $J_H$  means that the hopping of an outer-shell electron between two Mn sites is affected by the relative alignment of the core spins, being maximal when the core spins are parallel and minimal when they are antiparallel. This results in the double-exchange interaction between the localized spins, the core  $t_{2g}$  orbital (S = 3/2) mediated by the hopping  $e_g$  orbital electron<sup>[16, 17, 18]</sup>. The insulating sate is antiferromagnetic and the metallic state is ferromagnetic. Highly polarized state of Mn<sup>3+</sup> and Mn<sup>4+</sup> spins as a ferromagnetic order is necessary to achieve the d.c. conductivity based on the collapsed CO state.

By analogy with the  $Pr_{0.65}Ca_{0.35}MnO_3$ , electrons at the  $3d \cdot t_{2g}$  state is excited to the  $3d \cdot e_g$  state by the photon injection ( $h_{\mathcal{V}} = 1.17$  eV). Above the  $T_{CAF}$ , this photo-excited electrons (photo-excited spin state) contribute to the ESR. Below the  $T_{CAF}$ , the activation energy 130 meV is required to get a photo-excited spin state due to some kind of collective mechanism. The present results open an intriguing possibility of collective photo-induced magnetism in the distorted perovskite chromates.

#### 4. SUMMARY

The photo-induced effect in the distorted perovskite chromates,  $La_{0.5}Pr_{0.5}CrO_3$  was investigated by the X-band (9.0 GHz) ESR under the photo injection with photon energy  $h_{\mathcal{P}} = 1.17$  eV which is near infrared region. The  $La_{0.5}Pr_{0.5}CrO_3$  shows the CAF transition at  $T_{CAF} \sim 261$  K and the magnetic domains with random orientation of ferromagnetic component in the CAF spin order below the  $T_{CAF}$ . During the photo injection, the ESR intensity increases dramatically around the  $T_{CAF}$ . The observed photo-induced ESR profiles retain Lorentzian curvature with center resonance magnetic field = 320 mT. The photoinduced ESR intensity increase gradually with a increase in temperature up to 270 K i.e. the CAF state and grow up dramatically above the  $T_{CAF}$  i.e. the paramagnetic state. This high  $T_{CAF}$  allows us to provide photo-magnetic functional devices operated at room temperature. This transient magnetization was with the characteristic thermal activation energy of 130 meV. By analogy with the  $Pr_{0.65}Ca_{0.35}MnO_3$ , electrons at the 3d- $t_{2g}$  state is excited to the 3d- $e_g$  state by the photon injection ( $h_{\nu} = 1.17 \text{ eV}$ ). Above the  $T_{CAF}$ , this photo-excited electrons (photo-excited spin state) contribute to the ESR. Below the  $T_{CAF}$ , the activation energy 130 meV is required to get a photo-excited spin state due to some kind of collective mechanism.

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