Physical and Magnetic Properties of La$_{0.5}$Ca$_{0.5}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ at Temperature in the Range of 10-100 K

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Abstract. We have successfully measured physical and magnetic properties of the La$_{0.5}$Ca$_{0.5}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ at temperature in the range of 10-100 K. Physical properties have covered electrical resistivity and specific heat. The properties, which serve as a function of temperature, were investigated by using Physics Properties Measurement System (PPMS) with and without an external magnetic field up to 8.5 Tesla. The magnetic structure was characterized using High-Resolution Powder Diffraction (HRPD) at room and low temperatures. Furthermore, the magnetization was measured by using Magnetic Properties Measurement System (MPMS) with the external magnetic field of 0-7 Tesla. In the temperature interval of 10-53 K, the resistivity of the sample increased with the increasing of external magnetic field. At temperatures $T < 53$ K, the samples were crystalline metal. This was revealed by fitting the graph $\ln R$ as a function of $1/T$. At temperatures $T > 53$ K, the sample was an insulator according to fittings $\ln R$ as a function of $1/T^{1/3}$. The result was also shown by the decreasing value of the resistivity of the sample. The transition temperature of the metal-insulator ($T_M$) decreased with the increasing of external magnetic field, i.e. from 60 K without an external magnetic field to 53 K with external magnetic field 8.5 Tesla. A coefficient electron specific heat and specific heat of spin wave increased, and phonon specific heat was relatively unchanged in the presence of an external magnetic field. Results of HRPD experiment were analyzed by using Fullprof program. At room temperature, the sample had the paramagnetic phase, while at low temperatures of 20 K it had antiferromagnetic phase. Temperature phase transition from the paramagnetic to antiferromagnetic phase or Neel temperature was around 225 K. However, the saturation magnetization of the sample was not observed.

Keywords: metal-insulator; transition temperature; specific heat; magnetic structure; paramagnetic-antiferromagnetic
1. Introduction
The compounds of perovskite manganite with doping Cu, \( \text{R}_{1-x}\text{A}_x\text{Mn}_{1-y}\text{Cu}_y\text{O}_3 \) are still attractive to some researchers at last decade [1-7]. Study on these materials has not reached any consensus yet, such as resistivity, the nature magnetoresistance, and magnetization. The previous study of the Cu-doped at \( \text{La}_{0.47}\text{Ca}_{0.53}\text{Mn}_{1-x}\text{Cu}_x \) with \( x = 0.13 \) is still not clear. This sample can be in the metal-insulator state according to the model Arrhenius and Mott-model. Separating in one model is difficult. The fitting \( \text{LnR} \approx \frac{1}{T} \) has the same result with the fit \( \text{LnR} \approx \frac{1}{T^{0.25}} \) [1]. All previous studies, however, show that the Cu-doped at Mn site can change the resistivity.

The Cu substitution resulting decline insulator-metal transition temperature is related to the primary mechanism of double exchange which can disrupt network \( \text{Mn}^{3+}\text{-O-}\text{Mn}^{4+} \) [3]. The Cu-doped can increase a number of ions \( \text{Mn}^{4+} \), so it will strengthen the interaction of super-exchange antiferromagnetic between Mn ions.

This paper discusses the influence of an external magnetic field in the range of 0-9 T on the resistivity, specific heat, and magnetic transition temperature of the \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3 \).

2. Experimental Method
A sample of \( \text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3 \) was prepared by using the conventional solid-state reaction method [1] from materials \( \text{La}_2\text{O}_3 \), \( \text{CaCO}_3 \), \( \text{MnO}_2 \), and \( \text{CuO} \) with purity above 99%. High energy milling (HEM) was used to mix these materials. The sample was heated at a temperature of 1350°C for 6 hours, after which it was milled again. Finally, it was kept at 1100°C for 24 hours. XRD was used to characterize the crystal structure. While, the homogeneity of the sample was carried out by using HRPD (\( \lambda = 1.8223 \)) in the Laboratory for Neutron Scattering BATAN, Serpong, Tangerang.

Resistance measurements at various temperatures and magnetic fields were characterized by using a Physical Properties Measurement System (PPMS) in four probe configurations. Polycrystalline powders were compressed into pellets of equal thickness for each sample types. The sample was then cut to \( \sim 7 \text{ mm} \) (length) by \( 3 \text{ mm} \) (width) where 4-probe carbon paste contacts were applied at an equally spaced distance from each other to minimize the resistance variation due to the geometry of the electrodes. Magnetization measurements were investigated by using a SQUID Magnetic Properties Measurement Systems (MPMS).

3. Results and Discussion
Plot a graph of resistivity as a function of temperature \( R(T) \), both without an external magnetic field and the external magnetic field up to 8.5 T can be seen in Figure 1. The sample without an external magnetic field, at a temperature of \( T < 53 \text{ K} \), shows that the increasing of the external magnetic field, the resistivity of the sample is also increasing following the crystals model of Arrhenius, where the sample is more fulfilling plot graph \( \text{Ln} R \sim 1/T \). But for the temperature \( T > 53 \text{ K} \), it shows the increasing of the external magnetic field that affects it decreases and is more in line with the model of Mott insulator \( \text{Ln} R \sim 1/(T^{0.25}) \) (see Figure 2 a-b). The results indicate that the metal-insulator transition temperature \( T_{\text{M0}} \) occurs at 53 K. Furthermore, there are changes in metal-insulator transition temperature \( T_{\text{M0}} \) for some value of the external magnetic field. Those values are 53 K, 55 K, 58 K and 60 K for the value of an external magnetic field of 8.5 T, 6 T, 3 T and 0 T, respectively.

A resistivity peak corresponding to the magnetic transition is present. There is a clear field-induced shift of maximum resistivity for all samples, that is from 58 K for magnetic field 3 T into 53 K for 8.5 T. In the double exchange mechanism, the mobility of the charge carrier \( e_g \) electrons improves if the localized spins are polarized. The applied field aligns the canted electron spin which should reduce the scattering of itinerant electrons with spins and thus the resistivity is reduced [8]. With the increasing value of the external magnetic field, metal-insulator transition temperature \( T_{\text{M0}} \) becomes lower. This can be explained that the magnetic field is able to rotate electron spins which are not parallel to become more aligned, so it will reduce the value resistivity of the sample. While at low temperatures,
the spins of electrons are relatively parallel. Due to the external magnetic field, it will have an impact on the activation energy $E_a$ of samples. The amount of activation energy is calculated by equation (1).

$$R = C \exp\left(\frac{E_a}{kT}\right)$$

(1)

![Figure 1](image1.png)

**Figure 1.** Resistivity vs temperature in applied magnetic field $H = 0, 3, 6, 8.5$ T.

![Figure 2](image2.png)

**Figure 2.** Plot graph (a) $\ln R - \frac{1}{T}$ dan (b) $\ln R - \frac{1}{T^{0.25}}$ for $H = 0$ T at the temperature $< 53$ K.

The amount of activation energy due to the influence of an external magnetic field is $1.64 \times 10^{-6}$, $1.53 \times 10^{-6}$, $1.21 \times 10^{-6}$, and $1.12 \times 10^{-6}$ eV to an external magnetic field of 0, 3, 6, and 8.5 T, respectively.
Where \( R \) is the electrical resistance, \( C = \) factor pre-exponential containing among others the concentration of charge-carrier, \( T = \) absolute temperature, \( k = \) Boltzmann's constant, and \( E_a = \) activation energy.

The results characterization using high-resolution powder diffraction (HRPD) can be seen in Figure 3. The X-ray diffraction data were successfully analyzed by using FullProf program. The results show that the sample classified as a single phase. At a temperature of 300 K, the sample categorized as paramagnetic, while at the temperature of 20 K is antiferromagnetic. The orientation of the magnetic spin of the AFM to the direction of the axis b and c can be seen in the Figure 4.

![Figure 3. Diffraction patterns from neutron scattering (a) at room temperature and (b) at low temperature (20 K)](image_url)

The lattice constants, Mn(Cu)-O bond length and distortion parameters at room temperature and low temperature (20K) can be shown in Table 1. The volume and the Mn(Cu)-O bond length decrease with the lowering of the temperature. This will lead to increase distortion at the position B, which literally lead to increase the concentration of Mn\(^{3+}\) or Cu\(^2+\) associated with the Jahn-Teller effect. The variation of the deformation of the octahedral (Mn(Cu)O\(_6\)) related to B places is quite complex [9]. The lattice parameter of Cu is very small at low temperatures. The parameter of Cu is not only in a state of Cu\(^{2+}\) but also Cu\(^{3+}\) where the radius of Cu\(^{3+}\) is 0.54 Å, smaller than the radius of Mn\(^{3+}\) (0.645 Å), but larger than the radius Mn\(^{4+}\) (0.53 Å).
Figure 4. The orientation of the magnetic spins at a temperature of 20 K.

Table 1. The lattice constants \((a, b, c)\), The Mn(Cu)-O distance, and Jahn-Teller distortion at \((S_d)\) 300 K and 20 K

| \(T\) (K) | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(V\) (Å\(^3\)) | Mn-O\(_1\) (Å) | Mn-O\(_2\) (Å) | Mn-O\(_3\) (Å) | \(<d>\) | \(S_d\) |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|-------|
| 300      | 5.4205  | 7.6334  | 5.4387  | 225.0374| 1.9365  | 1.9408  | 1.9488  | 1.9420  | 6.502.10\(^{-3}\) |
| 20       | 5.4341  | 7.5394  | 5.4602  | 223.7022| 1.736   | 1.927   | 2.1466  | 1.9365  | 2.122.10\(^{-1}\) |

Generally, the specific heat can be calculated by equation

\[
C(T) = \gamma T + \beta_3 T^3 + \beta_5 T^5 + \delta T^n + \alpha T^2
\]

\[(2)\]

Where \(\gamma T\) is the electronic specific heat, \(\beta_3 T^3 + \beta_5 T^5\) is the phonon specific heat, \(\delta T^n\) is the specific heat of the spin wave \((n = 3/2\) for ferromagnetic spin wave, \(n = 2\) for antiferromagnetic spin wave), and \(\alpha T^2\) is the specific heat of the hyperfine structure [10]. Plot a graph of specific heat as a function of temperature \(C(T)\), both without an external magnetic field and the external magnetic field 9 T can be seen in Figure 5. From the analysis of the results of neutron scattering, it was found that the magnetic structure of the sample is antiferromagnetic, so \(n = 2\). From our experiments, the results of fitting of the data, without the magnetic field and the magnetic field 9 T can be seen in Table 2.

Our experiments showed that the coefficient of electronic specific heat \(\gamma\) without applied magnetic field is 11.6 mJ.mol\(^{-1}\).K\(^{-2}\), whereas the application of a magnetic field 9 T is resulting \(\gamma\) value by 78 mJ.mol\(^{-1}\).K\(^{-2}\). The resulting value of \(\gamma\) without the magnetic field, not much different from that produced by Z.Han et al. at 15 mJ.mol\(^{-1}\).K\(^{-2}\) [10]. The value of \(\gamma\) is related to electronic energy state density around the Fermi energy \(\gamma = (\pi^2/3)k_B^2N(E_F)\). The electronic energy state density around the Fermi energy is \(N(E_F) = 2.97 \times 10^{24}\) eV\(^{-1}\).cm\(^{-3}\) without magnetic field and 1.99 \(\times 10^{25}\) eV\(^{-1}\).cm\(^{-3}\) with external magnetic field 9 T. Of the value of \(\beta\), we can determine the Debye temperature \(\theta_0\) by using equation

\[
\theta_0 = (12\pi^2 pR/5\beta)^{1/3}
\]

\[(3)\]

Where \(R = \) Ideal gas constant, \(p = 5\) is the number of atoms per formula unit. We found the Debye temperature is 460 K.

The sample magnetization of La\(_{0.5}\)Ca\(_{0.5}\)Mn\(_{0.9}\)Cu\(_{0.1}\)O\(_3\) that measured in zero-field cooling (ZFC), field-cooled cooling (FCC), and field-cooled warming (FCW) at 2 mT can be seen in Figure 6. It appears that the curve FCC and ZFC are irreversible. It is as a consequence of the magnetic anisotropy of the compound. The antiferromagnetic transition temperature \((T_N)\) and the charge-ordered antiferromagnetic transition temperature \((T_{CO})\) measured on cooling were obtained from the maximum
of the low-field 2 mT. In the ZFC curve, the peak occurs at temperatures around 225 K. This indicates
the Neel temperature $T_N$, the phase transition temperature between the paramagnetic to antiferromagnetic phase occurs around this temperature. The $T_{CO}$ transition temperature is around 115 K. The heating and cooling M(T) curves display a small hysteresis close to the $T_N$. Probably this hysteresis is a consequence of the mixed character of the sample. We suspect there is a cluster ferromagnetic (FM) trapped in the cluster antiferromagnetic (AFM). At lowest temperature, a small anomaly in the M(T) curves marks the antiferromagnetic ordering, in complete agreement with the scan of neutron diffraction data.

Figure 5. The specific heat versus temperature curve of La$_{0.5}$Ca$_{0.5}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ under different magnetic field 0 T and 9 T at a temperature in the range of 10 K-100 K.

**Table 2.** Parameters under different magnetic fields fitting

| $H$ (T) | $\gamma$ (J.mol$^{-1}$.K$^{-2}$) | $\beta_1$ (J.mol$^{-1}$.K$^{-4}$) | $\beta_3$ (J.mol$^{-1}$.K$^{-6}$) | $\delta$ (J.mol$^{-1}$.K$^{-8}$) | $\alpha$ (J.mol$^{-1}$.K$^{-1}$) |
|--------|-----------------|---------------------|-------------------|---------------------|------------------|
| 0      | $1.16 \times 10^{-2}$ | $10^4$              | $10 \times 10^9$  | $3.4 \times 10^3$  | $1.4 \times 10^3$ |
| 9      | $7.8 \times 10^{-2}$ | $10^4$              | $9 \times 10^9$   | $3.5 \times 10^3$  | $1.4 \times 10^3$ |

Figure 7 shows the magnetization data M(H) of the sample measured at 120 and 140 K. It can be revealed that the isothermal Magnetization the data at 120 and 140 K is matched very well. The results of these two measures, both not saturated even though the external magnetic field up to 7 T. At temperature 120 K and 140 K, the value of $M$ rises slowly up to the value of the magnetic field 5 T, but to a temperature of 120 K, it began to appear hysteresis loop, indicating an increase in the value of the magnetic moment [1].

Figure 6. (a). ZFC, FCC, and FCW magnetization of La$_{0.5}$Ca$_{0.5}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ as a function of temperature. (b) The curve of susceptibility as a function of temperature.
Figure 7. Magnetization as a function of field of La_{0.5}Ca_{0.5}Mn_{0.9}Cu_{0.1}O_3 sample at temperature 120 K and 140 K.

4. Conclusions
The effect of external magnetic field on physical and magnetic properties of La_{0.5}Ca_{0.5}Mn_{0.9}Cu_{0.1}O_3 has been studied. The transition temperature of the metal-insulator $T_{MI}$ decreased with the increasing external magnetic field. While at a temperature of less than 53 K, the samples followed the model of Arrhenius. However, at the temperatures higher than 53 K, the samples followed the model of Mott-insulator. A coefficient of electronic specific heat $\gamma$ increased quite dramatically in the presence of an external magnetic field 8.5 T. At room temperature the samples were paramagnetic, while at low temperatures were antiferromagnetic. The transition temperature between the paramagnetic phase to the antiferromagnetic phase, referred to the Neel temperature $T_N$ of about 225 K.

5. References
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