Density-Driven Resistance Response in $MnS_2$: Theory

Komal Kumari*, Raman Sharma* and Navinder Singh**

*Department of Physics, Himachal Pradesh University,
Shimla, India, Pin:171005.
**Physical Research Laboratory, Ahmedabad,
Gujarat, India, Pin: 380009.

komal.phyhp@gmail.com; raman.sharma@hpuniv.ac.in; navinder@prl.res.in

Abstract

A colossal insulator-to-metal transition in high-spin pyrite phase of $MnS_2$ has been experimentally observed [1]. There are two possibilities behind this colossal insulator-to-metal transition: (1) migration of $Mn$ electrons to unoccupied $S_2^{-2}$ antibonding states under pressure which leads to conducting ligand states and hence metallic transition, and (2) possibility of band crossing transition. We have analyzed this experimental observation theoretically using a toy statistical model and found that the transition is due to the migration of electrons from the transition metal ions to the ligand sites (i.e. the possibility (1)). The calculated resistivity compares well with the experimental data within the fitting parameters of the model.

I Introduction

Pressure-induced insulator-to-metal transition has been experimentally observed in pyrite-structured mineral $MnS_2$[1][3]. $MnS_2$ is a high spin ($S_{Mn} = \frac{5}{2}$) transition metal chalcogenides insulator, which undergoes to metallic state following a colossal drop in resistivity (order $\sim 10^8\Omega$) under pressure($\simeq 12GPa$). At very high pressure ($P \gtrsim 36GPa$) it is a low spin ($S_{Mn} = \frac{1}{2}$) arsenopyrite ($a-MnS_2$). The $a-MnS_2$ shows insulation type resistive behaviour ($\rho(T)$) increases as tempertaure decreases.

In ref. [1] authors have proposed two mechanisms behind the observed transition. First one is that the metallic state arises when unoccupied disulfide $S_2^{-2} \sigma_{3p}^*$ antibonding states becomes partly filled due to migration of $d$ electrons from $Mn$ to $S$. The second possibility is due to band crossing transition wherein occupied ligand $p$ band merges with the unoccupied metal $d$ band [4][5]. It helps the conduction band to migrate below the Fermi level near the $\Gamma$ point. This leads to the conducting behaviour of the system.

Under very high pressure up to $\sim 36GPa$, $MnS_2$ reveals a low spin state transition into the dense arsenopyrite phase accompanied by a giant volume collapse [6][10]. This high density phase promotes electron localization effect and breaks the conduction. This leads to
We consider localized electrons in \( Mn \) \( d \) orbitals which migrate to conducting ligands \( S_2^2^- \) sites under pressure. In the next section we present the mathematical formulation of our model.

### II Mathematical Formulation

We consider the \( N \) number of sites per unit volume on a three dimensional lattice. We assume single unpaired electron on each lattice site (this corresponds to localized electrons in \( Mn \) \( d \) orbitals). Let \( J \) is the amount of energy cost to localize a given electron at a given site. If \( n \) out of total \( N \) electrons are in localized states (and \( N - n \) will be in the itinerant ligand sites), then \( n \) electrons cost \( Jn \) amount of energy to remain in localized sites. We write the canonical partition function for localized electrons as

\[
Z_n = \frac{N!}{n!(N-n)!} e^{-\beta Jn}.
\]

Here \( \beta = \frac{1}{k_B T} \) is the inverse temperature. The grand partition function for the system is

\[
Q = \sum_{n=0}^{N} Z_n e^{\beta \mu n},
\]

where \( \mu \) is the chemical potential. On substituting \( Z_n \) from (1) in (2), the grand partition function becomes

\[
Q = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} e^{\beta n(\mu - J)} = (1 + e^{\beta(\mu - J)})^N.
\]

Now the average number of the localized electrons is given by

\[
N_{\text{Loc}} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log(Q) = N \frac{e^{\beta(\mu - J)}}{(1 + e^{\beta(\mu - J)})}.
\]

The number of itinerant electrons can be written in the form \( N_{\text{iti}} = N - N_{\text{loc}} \):

\[
N_{\text{iti}} = N - N \frac{e^{\beta(\mu - J)}}{(1 + e^{\beta(\mu - J)})} = \frac{N}{(1 + e^{\beta(\mu - J)})}.
\]

These itinerant electrons form a Fermi sphere. Therefore in 3D:

\[
N_{\text{iti}}(T) = \frac{2}{V} \sum_k f_k = \frac{2}{(2\pi)^3} \int \frac{d^3 k}{e^{\beta(\epsilon - \mu)} + 1} = \frac{8\pi}{(2\pi)^3} \int_0^\infty \frac{k^2 dk}{e^{\beta(\epsilon - \mu)} + 1}.
\]
replacing \( k \) integral with energy \( \epsilon (k^2 = \frac{2me}{\hbar^2}) \), we obtain

\[
N_{iti}(T) = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \int_0^\infty \frac{\sqrt{\epsilon}d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}.
\]

(7)

The energy integral can be computed as

\[
N_{iti}(T) = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \left\{ \int_0^\mu \sqrt{\epsilon}d\epsilon + \int_\mu^\infty \frac{\sqrt{\epsilon}d\epsilon}{e^{\beta(\epsilon-\mu)}} \right\}.
\]

(8)

Under the relevant low temperature condition \( T \to 0, \beta \to \infty \) it simplifies to

\[
N_{iti}(T) = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \left\{ \frac{2}{3} \mu^3 + \frac{\sqrt{\mu}}{\beta} + \frac{\sqrt{\pi}e^{\beta\mu}}{2\beta^2} \text{erf}(\sqrt{\beta\mu}) \right\}.
\]

(9)

Now, the chemical potential can be obtained from the above equation and using equation (5) for \( N_{iti}(T) \):

\[
\frac{N}{(1 + e^{\beta(\mu-J)})} = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \left\{ \frac{2}{3} \mu^3 + \frac{\sqrt{\mu}}{\beta} + \frac{\sqrt{\pi}e^{\beta\mu}}{2\beta^2} \text{erf}(\sqrt{\beta\mu}) \right\}
\]

(10)

The above expression can be computed numerically to find \( \mu \) for given values of \( T, J, \) and \( N \).

Figure 1 shows \( \mu \) as a function of \( J \).

Figure 1: Presents chemical potential as a function of \( J \) at \( T = 2.0K \)

Our aim is to study the dependence of resistivity (\( \rho \)) on \( J \). We assume that the resistivity is given by the Drude-Lorentz model \( \rho(J) = \frac{m}{N_{iti}(J)e^{\beta\mu}} \). As \( N_{iti}(J) \) has dependence on \( J \), the change in \( J \) leads to change in resistivity. The local repulsion parameter \( J \) is pressure dependent. Under pressure there is a volume collapse and bond lengths (lattice parameters) decrease. This shorter lattice parameters leads to more local repulsion thus larger \( J \). In general there could be a complex dependence of \( J \) on pressure i.e. \( P = f(J) \). In our model we consider a linear approximation and set \( P = \alpha J \), where \( \alpha \) is a constant to be determined by
comparing the model with the experiment. We give the following justification for this linear dependence. Experiments\textsuperscript{[1]} show that under maximum pressure of 36\textit{GPa} the volume reduces by 20\% and hence the lattice parameter is reduced roughly by 6\%. Now the dependence of \( J \) on lattice parameter (\( a \)) can be roughly represented by

\[
J(\delta a) \sim \frac{1}{4\pi c_0 e_r} \left( \frac{q_1 q_2}{a + \delta a} \right) \sim k_1 \frac{\delta a}{a} + k_2,
\]

where \( k_1 \) and \( k_2 \) are constant and \( q_1 \) and \( q_2 \) are charges on adjacent ions. Thus in the leading order approximation we can set \( J \sim \delta a \). Therefore under a very small change (\( \delta a \)) in the lattice parameter, the dependence of \( J \) on \( a \) can be taken as linear. This motivates our assumption \( P = \alpha J \). With this assumption we compute \( \rho \) and compares it with the experimental data.

### III Experimental Comparison

Experimental data is obtained by digitizing the data in fig 1(a) of reference\textsuperscript{[1]}. We normalize the experimental data as \( \frac{\rho(P)}{\rho(0)} \) as we are interested in the pressure evolution of resistivity not absolute magnitude. The data is shown with the solid green line in figure \textsuperscript{2}

![Figure 2: Comparison of the present theory with the experimental data of MnS\textsubscript{2}](image)

We compute the resistivity from the formula \( \rho(J) = \frac{m}{N} \tau \) where \( P = \alpha J \). By treating \( \alpha \) as our fitting parameter we plot \( \rho(P) \) in figure\textsuperscript{2} (dashed red line). We use \( \tau = 10\text{femtosec} \) (a typical value of scattering rate in metals). Best fitting of our model with data corresponds to \( \alpha = 76.92 \text{GPa/eV} \). This leads to the validation of our model within the above mentioned assumption.

### IV Conclusion

Our simple statistical toy model which describes the localized electron to itinerant electron transition with the change of local repulsion parameter can qualitatively explain the mechanism of colossal resistive transition in \( \text{MnS}_2 \). Our model calculation shows that it is the migration of
Mn electrons to unoccupied $S_2^2$- antibonding states under pressure which leads to conducting ligand states and hence the metallic transition.

References

[1] Dylan Durkee, Nathan Dasenbrock-Gammon, G. Alexander Smith, Elliot Snider, Dean Smith, Christian Childs, Simon a.J. Kimber, Keith V. Lawler, Ranga P. Dias and Ashkan Salamat Physical Review Letters 127, 016401 (2021).

[2] Simon A. J. Kimber, Ashkan Salamat, Shaun R. Evans, Harald O. Jeschke, Kaliappan Muthukumar, Milan Tomić, Francesc Salvat-Pujol, Roser Valentí, Maria V. Kaisheva, Ivo Zizak, and Tapan Chatterji PNAS April 8, 111 14, 5106-5110, (2014).

[3] Dylan Durkee, Dean Smith, Raffaella Torchio, Sylvain Petitgirard, Richard Briggs, Innokenty Kantor, Shaun R. Evans, Tapan Chatterji, Tetsuo Irifune, Sakura Pascarelli, Keith V. Lawler, Ashkan Salamat, Simon A.J. Kimber, Journal of Solid State Chemistry, 269, 540-546, (2019).

[4] Q.Y. Chen etal, Phy. Rev. B 97, 155155 (2018).

[5] Kristin Persson, Gerbrand Ceder, and Dane Morgan Phys. Rev. B 73, 115201 (2006).

[6] T. Chattopadhyay and H.G. von Schnering and W.A. Grosshans Physica B+C, 139-140, 305-307, 1986.

[7] M A Timirgazin , P A Igoshev, A K Arzhnikov, V Yu Irkhin, Journal of Physics: Condensed Matter, 28, 505601 (2016).

[8] G. Brostigen and A. Kjekshus, Acta Chem. Scand. 24, 2993 (1970).

[9] A. Rohrbach, J Hafner, and G. Kresse, J. Phys. Condens. Matter 15, 979 (2003).

[10] Allen JW, Martin R M. Phys Rev Lett. 4 9:1106–1110 (1982).

[11] Navinder Singh arXiv:2105.00688v1 [Cond-mat.str-el] (2021).

[12] R. Kubo, Statistical mechanics-an advanced course with problems an solutions, North-Holland publishing Company, Amsterdam (1971).