Diagnosis of transport properties in Ferromagnets

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(Dated: November 21, 2018)

The ionization energy based resistivity model with further refinements from spin-disorder scattering and polaronic effect is derived so as to capture the mechanism of both spin independent and spin-assisted charge transport in ferromagnets. The computed $T_{\text{crossover}}$ below $T_C$ and carrier density in Ga$_{1-x}$Mn$_x$As ($x = 6-7\%$) are 8-12 K and 10$^{19}$ cm$^{-3}$, identical with the experimental values of 10-12 K and 10$^{19}$-10$^{20}$ cm$^{-3}$ respectively. The calculated charge densities for Mn$_{0.02}$Ge$_{0.98}$ and La$_{1-x}$Ca$_x$MnO$_3$ ($x = 10-20\%$) are 10$^{19}$ cm$^{-3}$ and 10$^{17}$ cm$^{-3}$ respectively.

PACS numbers: 75.70.-i; 71.30.+h; 72.15.Rn; 75.50.Pp
Keywords: Ferromagnets, Fermi-Dirac statistics, Ionization energy, Resistivity model

1. Introduction

Diluted magnetic semiconductors (DMS) have the tremendous potential for the development of spintronics and subsequently will lay the foundation to realize quantum computing. In order to exploit the spin assisted charge transport, one needs to understand the transport mechanism such as the variation of resistivity with temperature and doping in both paramagnetic and ferromagnetic phases. A wide variety of the magneto-electronic properties based on doping and Mn’s valence state in manganites were reported to understand the transport properties below $T_C$ in the well known and extensively studied FM manganites as pointed out by Mahendiran et al. The resistivity ($\rho(T)$) above $T_C$ for manganites is found to be in an activated form described by the equation

$$\rho(T > T_C) = \rho_0 \exp \left( \frac{E_a}{k_B T} \right). \quad (1)$$

$E_a$ is the activation energy, $\rho_0$ and $k_B$ denote the residual resistivity at $T \gg E_a$ and Boltzmann constant respectively. In the FM phase, the influence of $M(T)/M_0$ is more pronounced than the electron-phonon ($e$-$ph$) contribution where the latter requires an overwhelmingly large coupling constant. Note that $M_0$ is the magnitude of magnetization at 0 K. Therefore, Mahendiran et al. have suggested that conventional mechanism namely, $e$-$ph$ scattering has to be put aside so as to explain the $\rho(T)$ for manganites below $T_C$. On the contrary, $\rho(T)$ with $e$-$ph$ involvement for DMS in the paramagnetic phase is given by

$$\rho(T > T_C) = C_1 + C_2 \left[ \exp (\Theta_{D}/T) - 1 \right]^{-1} \frac{1}{k_B T} \ln \left[ 1 + \exp ((E_m - E_f)/k_B T) \right]. \quad (2)$$

The term, $C_2/[\exp(\Theta_D/T) - 1]$ takes care of the $e$-$ph$ contribution. $\Theta_D$, $E_f$, $E_m$, $C_1$ and $C_2$ represent the Debye temperature, Fermi level, mobility edge and numerical constants respectively. The $\rho(T)$ in the FM phase based on the spin disorder scattering as derived by Tinbergen-Dekker is given by

$$\rho_{SD}(T < T_C) = \frac{(m^*_{e,h})^{5/2} N(2E_F)^{1/2}}{\pi(n,p)^{1/2} \epsilon^2 \hbar^4} J_{ex}^2 \times \left[ S(S+1) - S^2 \left( \frac{M_{TF}(T)}{M_0} \right)^2 - S \left( \frac{M_{TF}(T)}{M_0} \right) \right].$$
\[ \rho^{-1} = \rho_{e,h}^{-1} + \rho_{se,sh}^{-1} = \left[ \frac{m^*_{e,h}}{(n,p)e^{2\tau_{se}}} \right]^{-1} + \left[ \frac{m^*_{e,h}}{(n,p)e^{2\tau_{SD}}} \right]^{-1}. \] (4)

\[ \tau_{SD} \] represents the spin disorder scattering rate. The carrier density for the electrons and holes \((n,p)\) based on iFDS are given by \([23, 24, 27, 28, 29, 30]\). Substituting \(1/\tau_e = AT^2\) (due to electron-electron interaction), Eqs. (3) and (5) or (6) into Eq. (4), then one can arrive at

\[ \rho_{e,se}(T) = \frac{AB \exp \left[ \left( E_I + E_F \right)/k_BT \right]}{AT^{3/2}|M_p(T, M_0)|^{-1} + BT^{-1/2}}. \] (7)

In which, \(A = \frac{[A_{e,h}/2e^2(m^*_{e,h})^{1/2}]|2\pi h^2/k_B|^{3/2}}{N(2E_F)^{1/2}J_{ex}^2/e^2h^2B}\) and \(\tau_{SD}^{-1} = [N(2E_F)^{1/2}(m^*_{e,h})^{3/2}/\pi^2h^2J_{ex}^2]_seM_p(T, M_0)\). \(A_{e,h}\) is the \(T\) independent electron-electron scattering rate constant. The \(E_I\) here takes care of the polaronic effect or more precisely, the electron-photon interaction. The empirical function of the normalized magnetization is given by

\[ M_p(T, M_0) = 1 - \frac{M_p(T)}{M_0}. \] (8)

Equation (8) is an empirical function that directly quantifies the influence of spin alignments in the FM phase on the transport properties of charge and spin carriers in accordance with Eq. (7). In other words, the only way to obtain \(M_p(T)\) is through Eq. (8). In fact, Eq. (8) is used to calculate \(M_{TB}(T)/M_0\) and \(M_K(T)/M_0\) by writing \(S(S + 1) - S^2(\frac{M_p(T)}{M_0})^2 - S(\frac{M_{TB}(T)}{M_0})\) tanh \([\frac{3T_C M_{TB}(T)}{2TS(S + 1)M_0}]\) = \(M_p(T, M_0)\) and \(S(S + 1) - S^2(\frac{M_K(T)}{M_0})^2 - S(\frac{M_K(T)}{M_0}) = M_p(T, M_0)\) respectively. Consequently, one can actually compare and analyze the
dependence of the scattering rates namely, $\tau$ and $\Delta$. The Greenisen (BG) formula \[31\], given by

$$\rho_h = \frac{A_h(m^*_h)^{3/2}}{2e^2} \left[ \frac{2\pi \hbar^2}{k_B} \right]^{3/2} T^{1/2} \exp \left[ \frac{E_I + E_F}{k_B T} \right].$$ \eqno(9)

$A_h$ is the $T$ independent electron-electron scattering rate constant. Equation (9) will be used to justify the importance of the term $J_{se}$ even if the resitivity is semiconductor-like in the FM phase. Note that, $m^* = m^*_e \approx m^*_h \approx (m^*_e m^*_h)^{1/2}$ is used for convenience. However, for FM, $m^*_e \neq m^*_h$, then one just has to use the relation, $m^* = m^*_e m^*_h/(m^*_e + m^*_h)$. Even in the usual consideration for the total conductivity, $\sigma = \sigma_{electron} + \sigma_{hole}$, some algebraic rearrangements can lead one to the relation, $\rho(T) \propto \exp(E_I/k_BT)/\exp(E_F/k_BT) + \exp(-E_F/k_BT)$, exposing the consistent effect of $E_I$ on transport properties.

3. Discussion

3.1. Temperature-dependent resistivity curves

 Resistivity versus temperature measurement ($\rho(T)$) is the most simplest and effective method to study the transport properties. In free-electron metals, the $\rho(T)$ curves are often exploited in order to deduce the $T$-dependence of the scattering rates namely, $\tau_{ee}$ and $\tau_{ep}$. Such behavior are well described by the Bloch-Grüneisen (BG) formula \[31\], given by

$$\rho_{BG} = \frac{128\pi m^* k_B T^5}{n e^2 \Theta_D^2} \lambda_{tr} \int_0^{\Theta_D/2T} \frac{x^5}{\sinh^2 x} dx. \eqno(10)$$

$\lambda_{tr}$ electron-phonon coupling constant, $n$ free electrons concentration. The approximation of $\tau_{ee}(T)$ and $\tau_{ep}(T)$ using Eq. (10) is valid basically because there are no other parameters that vary with $T$, apart from the said scattering rates. In fact, by utilizing the BG formula, one can reliably estimate that $\tau_{ee}(T) \propto T^{-2}$ while $\tau_{ep}(T) \propto T^{-3 + \gamma_{ep}}$ for any experimentally viable $\Theta_D$.

On the other hand, the metallic phenomenon observed in the ferromagnetic-metallic (FMM) phase below $T_C$ in ferromagnets (FM) cannot be characterized as Fermi gas. Therefore, it is rather incorrect to extract $\tau_{ee}(T)$, $\tau_{ep}(T)$ and $\tau_{magnons}(T)$ from the $\rho(T < T_C)$ curves in FM. Experimental evidences based on the photoemission, X-ray emission/absorption and extended X-ray emission fine structure spectroscopy have exposed the polaronic effect even at $T < T_C$ or in the FMM phase \[32\]. Consequently, the charge density ($n$) in FMM phase is not $T$ independent as one would anticipate for the free-electron metals (Fermi-gas). In addition, spin related mechanisms, like magnons and spin disorder scattering can be correctly represented with the normalized magnetization function, $M(T, M_0)$. It is quite common to employ Matthiessen’s rule ($\tau^{-1} = \sum_i \tau_i^{-1}$) as opposed to the total current rule ($\tau = \sum_i \tau_i$) and write the resistivity below $T_C$ in the form of

$$\rho(T) = \rho_0 + \sum_i A_i T^{\alpha_i}. \eqno(11)$$

The $i$ here indicates the types of $T$-dependent scattering rate that contribute to the resistivity and $A$ is a $T$ independent constant. $\rho_0$ is the $T$-independent scattering rate that originates from the impurities as $T \to 0$ K. The critical issue here is not about the Matthiessen’s rule, but on the validity of Eq. (11) in non-free-electronic phase. Importantly, the $T$-dependent structure of Eq. (11) that actually have enabled one to reliably calculate $\tau_{ee}(T)$ and $\tau_{ep}(T)$ as $A_{ee} T^2$ and $A_{ep} T^{3 + \gamma_{ep}}$ respectively. Equation (11) is extremely popular and it is applied indiscriminately to determine the $T$-dependence of a wide variety of scattering rates in FMM phase, while the correctness of such determination is still unclear and varies from one researcher to another \[18, 33, 34\]. It is important to realize that only a free-electronic FMM phase at $T < T_C$ will justify the analysis based on Eq. (11). The influence of polaronic effect and magnetization function (the variation of $M(T)/M_0$ with $T$) reinforces the $T$-dependence of charge density, which point towards the inapplicability of Eq. (11) in FMM phase.

3.2. Ga$_{1-x}$Mn$_x$As

The resistivity measurements \[17\] and its fittings based on Eqs. (7) and (9) are shown in Fig. 1a) and b) respectively for Ga$_{1-x}$Mn$_x$As. One needs two fitting parameters ($A$ and $E_I$) for $\rho(T > T_C)$ and another two ($B$ and $M_0(T, M_0)$) for $\rho(T < T_C)$. All the fitting parameters are listed in Table I. Note that $S = 1$ and $5/2$ are employed for the fittings of $M_0(T)/M_0$ while $T_C$ and $T_{crossover} = T_{cr}$ were determined from the experimental resistivity curves. The deviation of $M_0(T)/M_0$ from the $M_{exp}/M_0$ increases with $S$ from 1 $\to$ 5/2. The $\rho(T)$ is found to increase with $x$ from 0.060 to 0.070 due to the mechanism proposed by Van Esch et al. \[17, 37\] and Ando et al. \[36\]. They proposed that neutral Mn$^{3+}$ acceptors that contribute to magnetic properties could be compensated by As, where for a higher concentration of
Mn, instead of replacing Ga it will form a six-fold coordinated centers with As (Mn$^{6+}$). These centers will eventually reduce the magnitude of ferromagnetism (FM) in DMS due to the loss of spin-spin interaction between Mn(3d$^5$) and h. iFDs based resistivity models also predicts that if one assumes Mn$^{2+}$ ($E_I = 1113$ kJmol$^{-1}$) or Mn$^{3+}$ ($E_I = 1825$ kJmol$^{-1}$) substitutes Ga$^{3+}$ ($E_I = 1840$ kJmol$^{-1}$), then $\rho(T)$ should further decrease with x, which is not the case here. Thus, iFDs also suggests that Mn$^{2+}$ or Mn$^{3+}$ do not substitute Ga$^{3+}$. Interestingly, the $T_C$'s observed in Ga$_{0.94}$Mn$_{0.06}$As (annealed: 370°C) and Ga$_{0.93}$Mn$_{0.07}$As (as grown) are 10 K and 12 K, which are identical with the calculated values of 8 K and 12 K respectively. Note here that $E_I + E_F = T_C$.

The calculated carrier density using $E_I$ + $E_F$ (8, 12 K), $m^*_h$ = rest mass and Eq. (6) is $2.4 \times 10^{19}$ cm$^{-3}$. Below $T_C$, spin alignments enhance the contribution from $J_{se}$ and reduces the exponential increase of $\rho(T)$. This reduction in $\rho(T)$ is as a result of dominating $J_{se}$ and the small magnitude of $E_I + E_F$ (8 K, 12 K), consequently its effect only comes at low T as clearly shown in Fig. 1a). The Ga$_{0.93}$Mn$_{0.07}$As samples after annealing at 370°C and 390°C do not indicate any FM (Fig. 1b). Thus the fittings are carried out with Eq. (9) that only requires two fitting parameters namely, $A$ and $E_I + E_F$ since $J_{se} = 0$ (there is no observable $T_C$) and/or $dM_s(T)/dM_0$ = 0 ($M_p(T, M_0)$ = constant). The exponential increase in Fig. 1b) for $\rho(T)$ is due to $\rho(T) + E_F$ from Eq. (9) with zilch $J_{se}$ contribution.

Figure 1c) and d) indicate the normalized magnetization, $M_s(T)/M_0$. Note that $M_{p,T,D,K}(T)/M_0$ is a fitting parameter that has been varied accordingly to fit $\rho(T < T_C)$. $M_p(T, M_0)$ is used to calculate $M_{p,T,D,K}(T)/M_0$ with $S = 1$. $M_{p,T,D,K}(T)/M_0$ is also compared with the experimentally determined $M_{exp}(T)/M_0$ as depicted in Fig. 1d). One can easily notice the inequality, $M_{T,D}(T)/M_0 > M_K(T)/M_0 > M_p(T)/M_0 > M_{exp}(T)/M_0$ from Fig. 1c) and d). As such, $M_p(T)/M_0$ from Eq. (9) is the best fit for the experimentally measured $M_{exp}(T)/M_0$. However, $M_p(T)/M_0$ is still larger than $M_{exp}(T)/M_0$, because resistivity measures only the path with relatively lowest $E_I$ and with easily aligned spins that complies with the principle of least action. On the contrary, the magnetization measurement quantifies the average of all the spins’ alignments.

### 3.3. La$_{1-x}$Ca$_x$MnO$_3$

Mahendiran et al. discussed $\rho(T < T_C)$ with respect to Eq. (1) and obtained the activation energy, $E_a = 0.16$ eV for $x = 0.1$ and 0.2 of La$_{1-x}$Ca$_x$MnO$_3$ samples at 0 T. Using Eq. (7) however, $E_I + E_F$ for the former and latter samples are calculated to be 0.12 and 0.11 eV respectively. The calculated carrier density using $E_I + E_F$ (0.12, 0.11 eV), $m^*_h$ = rest mass and Eq. (9) is approximately $10^{17}$ cm$^{-3}$. In the presence of $H = 6$ T, $E_I + E_F$ is computed as 0.0776 eV for $x = 0.2$ that subsequently leads to $\rho = 10^{18}$ cm$^{-3}$. It is proposed that the activated behavior for $\rho(T > T_C)$ is due to electronphonon interaction or rather due to the polaronic effect ($E_I$). The fittings are shown in Fig. 2a) and b) while its fitting parameters are listed in Table 1. Theoretically, Ca$^{2+}$ ($E_I = 868$ kJmol$^{-1}$) < La$^{3+}$ ($E_I = 1152$ kJmol$^{-1}$), therefore $\rho(T)$ is expected to decrease with Ca$^{2+}$ doping significantly. On the contrary, only a small difference of $E_I + E_F$ between $x = 0.1$ (0.12 eV) and 0.2 (0.11 eV) is observed due to Mn$^{4+}$’s compensation effect. The quantity, Mn$^{4+}$ increased 6% from $x = 0.1$ (19%) to 0.2 (25%) $E_I$. Ideally, the difference of $E_I$ between Ca$^{2+}$ and La$^{3+}$ is 1152 − 868 = 284 kJmol$^{-1}$. As a result of compensation with 6% Mn$^{3+}$$-$- Mn$^{4+}$ ($E_I = 4940$ kJmol$^{-1}$), the actual difference is only 284 − 0.81(1825) + 0.19(4940) − 0.75(1825) − 0.25(4940) = 97 kJmol$^{-1}$. This calculation simply exposes the compensation effect.

At 6 T, La$_{0.8}$Ca$_{0.2}$MnO$_3$ indicates a much lower resistivity (Fig. 2b)). The result that larger $H$ giving rise to overall conductivity is due to relatively large amount of aligned spins that eventually gives rise to $J_{se}$. Hence, $E_I + E_F$ at 6 T (78 meV) is less than $E_I + E_F$ at 0 T (112 meV). Figure 2c) and d) depict the calculated $M_{exp}(T)/M_0$ with $S = 1$ and $M_{exp}(T)/M_0$ for $x = 0.2$ respectively. The calculated $M_{TD}(T)/M_0$ is dropped for La$_{1-x}$Ca$_x$MnO$_3$ since $M_K(T)/M_0$ seems to be a better approximation than $M_{TD}(T)/M_0$ as indicated in Fig. 1c) and d). The discrepancy between $M_p(T)/M_0$ and $M_{exp}(T)/M_0$ still exists even though Eq. (7) reproduces $\rho(T)$ at all T range accurately. Again, this incompatibility is due to the principle of least action as stated earlier. In addition, the mangenates’ charge transport mechanism below $T_C$ is also in accordance with Eq. (7) because the term, $M_p(T, M_0)$ handles the exchange interactions’ complexities separately for DMS and maneganites. For example, one can clearly notice the different type of discrepancies between DMS and mangenates by comparing the empirical function, $M_s(T)/M_0$ ($\alpha = \rho$, exp) between Fig. 1d) and Fig. 2d). Hence, Eq. (7) is suitable for both types of ferromagnets, be it diluted or concentrated.

### 3.4. Mn$_x$Ge$_{1-x}$

The Mn$_x$Ge$_{1-x}$ FMS with homogeneous Mn concentration has been grown using low-T MBE technique. The Mn$_x$Ge$_{1-x}$ was found to be a p-type with carrier density in the order of $10^{19}$−$10^{20}$ cm$^{-3}$ for 0.006 $\leq x \leq 0.035$ as measured by Park et al. The resistivity measurements and its fittings based on Eq. (7) are shown in Fig. 3a). Here, $E_I + E_F$, $A$ and $B$ have been floated while $M_p(T, M_0)$ is constrained to reduce with $T$ in order to fit the experimental $\rho(T, x = 0.02)$. The absence of
the Curie-Weiss law in the $\rho(T, x = 0.02)$ curve is due to insufficient number of aligned spins that eventually leads to a relatively small $J_{ex}$, which in turn, is not able to produce the metallic conduction below $T_C$. This scenario is also in accordance with the measured $M_{exp}(T)$ where, only $1.4-1.9 \mu_B$/Mn atom contributes to ferromagnetism as compared with the ideal value of $3.0 \mu_B$/Mn atom. In other words, only 45-60% of Mn ions are magnetically active. It is found that $E_I + E_F = 15$ K from the $\rho(T)$ fitting for Mn$_{0.02}$Ge$_{0.98}$. Subsequently, one will be able to calculate the hole concentration as $2.38 \times 10^{19}$ cm$^{-3}$ using Eq. (9) and $m^*_h = \text{rest mass}$, which is remarkably in the vicinity of the experimental value $22$, $10^{19} - 10^{20}$ cm$^{-3}$. Interestingly, the semiconductor-like behavior of $\rho(T, x = 0.02)$ below $T_C$ is not exponentially driven as the value of $E_I + E_F$ is very small (15 K) to be able to contribute significantly above 15 K. Rather, it is the $T$-dependence of Eq. (7) determines $\rho(T, x = 0.02)$ below $T_C$. To see this clearly, one can actually approximate the experimental $\rho(T, x = 0.02)$ with a mathematical function given by $\rho = -21.711 \times \ln T + 148.47$ (not shown).

In this computation, the $lnT$ behavior is the approximate version for the $T$-dependence of Eq. (7). Another obvious proof is the inability of Eq. (9) to represent the experimental $\rho(T, x = 0.02)$. The plot using Eq. (9) is also shown in Fig. 4(a) with $A_h = 1.8$ and $E_I + E_F = 80$ K that eventually give $p = 1.92 \times 10^{19}$ cm$^{-3}$. However, in the absence of $J_{xc}$ term, Eq. (9) is inadequate to capture the $T$-dependence of $\rho(T, x = 0.02)$ in the FM phase.

The pronounced effect of $M_{\rho}(T, M_0)$ can be noticed by comparing the calculated plots between Eq. (7) and Eq. (9) with additional constraint, $dM_{\rho}(T)/dT = 0$ as indicated in Fig. 3(a). Recall that $M_{\rho}(T, M_0)$ is varied with $T$ to fit the experimental $\rho(T, x = 0.02)$ in compliance with Eq. (7). Furthermore, $\rho(T, x = 0.02)$ is found to decrease with $x$ from 0.016 to 0.02 while $\rho(T, x = 0.02)$ remains identical with $\rho(T, x = 0.033)$. This type of transition can be readily evaluated with Eq. (7). Firstly, notice the large increase in room temperature $p$ from $10^{14}$ cm$^{-3}$ (upper limit) for pure Ge to $10^{19}$ cm$^{-3}$ (lower limit) for a mere 2% Mn substituted Mn$_{0.02}$Ge$_{0.98}$, which gives rise to a rapid decrease of $\rho(T, x)$. The average $E_{1s}$ for Mn$^{2+}$, Mn$^{3+}$ and Ge$^{4+}$ are computed as 1113, 1825 and 2503 kJmol$^{-1}$ respectively. According to iFDS, Mn substitution into Ge sites will reduce the magnitude of $\rho(T)$ since $E_I$ (Ge$^{4+}$) $> E_I$ (Mn$^{4+}$) $> E_I$ (Mn$^{3+}$), regardless of $dM(T)/dT = 0$ or $dM(T)/dT \neq 0$. Such behavior has been observed experimentally $22$ whereas, $\rho(T, x = 0.009) > \rho(T, x = 0.016) > \rho(T, x = 0.02)$. This scenario indicates that the holes from Mn$^{2+}$-$3^{+}$+ is kinetically favorable than the intrinsic holes from Ge$^{4+}$. It is also found experimentally that $\rho_{rt}(x = 0.009) < \rho_{rt}(x = 0.016)$ as a result of the variation of $T$ independent scattering rate constants ($A$ and $B$). Surprisingly however, $\rho(T, x = 0.02) \approx \rho(T, x = 0.033)$, which suggests that $A$, $B$ and $T$-dependence of $M_{exp}(T)/M_0$ are identical. Using iFDS, one should get $\rho(T, x = 0.02) > \rho(T, x = 0.033)$ and $|A, B| = 0.02 > |A, B| = 0.033$. Meaning, the additional Mn substitution ($0.033 - 0.02 = 0.013$) may not have substituted Ge, instead it could have formed a well segregated impurity phase that eventually contributes to the higher magnitudes of $A$ and $B$ ($|A, B| = 0.02 \approx |A, B| = 0.033$), and consequently does not interfere with the $M_{exp}(T)/M_0$. Notice that the formation of impurity phase is quite common in any system, including Ga$_{1-x}$Mn$_x$As DMS with strictly limited Mn solubility. On the other hand, the normalized magnetization, $M_{K_p,exp}(T)/M_0$ for Mn$_{0.02}$Ge$_{0.98}$ have been plotted in Fig. 3(b). One can notice the relation, $M_K(T)/M_0 > M_p(T)/M_0 > M_{exp}(T)/M_0$ from Fig. 3(b). Again, $M_p(T)/M_0 > M_{exp}(T)/M_0$ is due to the ability of both $J_e$ and $J_{xc}$ to follow the easiest path. Additionally, the $T$-dependence of $M_{exp}(T)$ is similar to Ga$_{1-x}$Mn$_x$As rather than the well established manganite ferromagnets, which reveals the possibility of multiple exchange interactions $17$ $22$ $32$. All the values of $E_I$ discussed above were averaged in generation with $E_I[X^{\pm\pm}] = \sum_{i=1}^{\pm\pm} E_{1s}$. Prior to averaging, the $1^{st}$, $2^{nd}$, $3^{rd}$ and $4^{th}$ ionization energies for all the elements mentioned above were taken from Ref. 37.

4. iFDS

Here, the Lagrange multipliers, degeneracy and the total energy requirement associated with $E_I$ in iFDS is discussed in detail. Both FDS and iFDS are for the half-integral spin particles such as electrons and holes. Its total wave function, $\Psi$ has to be antisymmetric in order to satisfy quantum-mechanical symmetry requirement. Under such condition, interchange of any 2 particles ($A$ and $B$) of different states, $\psi_i$ and $\psi_j$ ($j \neq i$) will result in change of sign, hence the wave function for Fermions is in the form of

$$\Psi_{i,j}(C_A, C_B) = \psi_i(C_A)\psi_j(C_B) - \psi_i(C_B)\psi_j(C_A). \quad (12)$$

The negative sign in Eq. (12) that fulfils antisymmetric requirement is actually due to one of the eigenvalue of exchange operator $38$, $P = -1$. The other eigenvalue, $P = +1$ is for Bosons. $C_A$ and $C_B$ denote all the necessary cartesian coordinates of the particles $A$ and $B$ respectively. Equation (12) is nothing but Pauli’s exclusion principle. The one-particle energies $E_{1s}, E_2, ..., E_m$ for the corresponding one-particle quantum states $q_1, q_2, ..., q_m$ can be rewritten as $(E_{1s} \pm E_{11}), (E_{1s} \pm E_{12}), ..., (E_{1s} \pm E_{1m})$. Note here that $E_{1s}$ is $E_{initial state}$. It is also important to realize that $E_{1s} + E_I = E_{electrons}$ and $E_{1s} - E_I = E_{holes}$. Subsequently, the latter $(E_{1s} \pm E_I)$ version where $i = 1, 2, ..., m$ with $E_I$ as an additional inclusion will be used to derive iFDS and its Lagrange
multipliers. This $\pm E_I$ is inserted carefully to justify that an electron to occupy a higher state $N$ from initial state $M$ is more probable than from initial state $L$ if condition $E_I(M) < E_I(L)$ at certain $T$ is satisfied. As for a hole to occupy a lower state $N$ from initial state $N$ is more probable than to occupy state $L$ if the same condition above is satisfied. $E_{is}$ is the energy of a particle in a given system at a certain initial state and ranges from $+\infty$ to $0$ for electrons and to $-\infty$ for holes. In contrast, standard FDS only requires $E_i(i = 1, 2, ..., m)$ as the energy of a particle at a certain state.

Denoting $n$ as the total number of particles with $n_1$ particles with energy $(E_{is} \pm E_I)_1$, $n_2$ particles with energy $(E_{is} \pm E_I)_2$ and so on implies that $n = n_1 + n_2 + \ldots + n_m$. As a consequence, the number of ways for $q_1$ quantum states to be arranged among $n_1$ particles is given as

$$P(n_1, q_1) = \frac{q_1!}{n_1!(q_1 - n_1)!}. \tag{13}$$

Now it is easy to enumerate the total number of ways for $q$ quantum states ($q = q_1 + q_2 + \ldots + q_m$) to be arranged among $n$ particles, which is

$$P(n, q) = \prod_{i=1}^{\infty} \frac{q_i!}{n_i!(q_i - n_i)!}. \tag{14}$$

The most probable configuration at certain $T$ can be obtained by maximizing $P(n, q)$ subject to the restrictive conditions

$$\sum_{i=1}^{\infty} n_i = n, \sum_{i} dn_i = 0. \tag{15}$$

$$\sum_{i} (E_{is} \pm E_I)n_i = E, \sum_{i} (E_{is} \pm E_I)dn_i = 0. \tag{16}$$

The method of Lagrange multipliers can be employed to maximize Eq. (15). Hence, a new function, $F(x_1, x_2, \ldots, \mu, \lambda, \ldots)$ is introduced and all its derivatives are set to zero

$$\frac{\partial F}{\partial x_n} = 0; \frac{\partial F}{\partial \mu} = 0; \frac{\partial F}{\partial \lambda} = 0. \tag{17}$$

As such, one can let the new function in the form of

$$F = \ln P + \mu \sum_{i} dn_i + \lambda \sum_{i} (E_{is} \pm E_I)dn_i. \tag{18}$$

After applying Stirling’s approximation, $\partial F/\partial n_i$ can be written as

$$\frac{\partial F}{\partial n_i} = \ln(q_i - n_i) - \ln n_i + \mu(E_{is} \pm E_I)_i = 0. \tag{19}$$

Thus, the Fermi-Dirac statistics based on ionization energy is simply given by

$$\frac{n_i}{q_i} = \frac{1}{\exp[\mu + \lambda(E_{is} \pm E_I)] + 1}. \tag{20}$$

Importantly, the total energy, $E$ in iFDS can be obtained from Eq. (16), which is

$$E = \sum_{i} (E_{is} \pm E_I)_i n_i$$

$$= \sum_{i} \frac{\hbar^2}{2m} [k_{is}^2 \pm k_i^2]_i n_i$$

$$= \frac{\hbar^2}{2m} [k_{is}^2 \pm k_i^2] = \frac{\hbar^2}{2m} k^2. \tag{21}$$

$k_I$ is the ionized state, and the $\pm$ sign is solely to indicate that the energy corresponds to electrons is $0 \rightarrow +\infty$ while $0 \rightarrow -\infty$ is for the holes, which satisfy the particle-hole symmetry. Consequently, Eq. (21) also implies that iFDS does not violate the degeneracy requirements. By utilizing Eq. (20) and taking $\exp[\mu + \lambda(E \pm E_I)] \gg 1$, one can arrive at the probability function for electrons in an explicit form as

$$f_e(k_{is}) = \exp \left[ -\mu - \lambda \left( \frac{\hbar^2 k^2}{2m} + E_I \right) \right]. \tag{22}$$

Similarly, the probability function for the holes is given by

$$f_h(k_{is}) = \exp \left[ \mu + \lambda \left( \frac{\hbar^2 k^2}{2m} - E_I \right) \right]. \tag{23}$$

The parameters $\mu$ and $\lambda$ are the Lagrange multipliers. $h = h/2\pi$, $h = $ Planck constant and $m$ is the charge carriers mass. Note that $E$ has been substituted with $h^2 k^2/2m$. In the standard FDS, Eqs. (22) and (23) are simply given by, $f_e(k) = \exp[-\mu - \lambda(h^2 k^2/2m)]$ and $f_h(k) = \exp[\mu + \lambda(h^2 k^2/2m)]$. Equation (15) can be rewritten by employing the 3D density of states (DOS) derivative, $dn = V(k_{is}^2) d(k_{is}/2\pi^2)$, Eqs. (22) and (23), that eventually give

$$n = \frac{V}{2\pi^2} e^{-\mu} \int_{0}^{\infty} k^2 \exp \left[ -\lambda \frac{h^2 k^2}{2m} \right] dk.$$
\[ E = \frac{V \hbar^2}{4m\pi^2} e^{-\mu(FDS)} \int_0^\infty k^4 \exp \left[ -\lambda \frac{\hbar^2 k^2}{2m} \right] dk \]

\[ = \frac{V \hbar^2}{4m\pi^2} e^{-\mu(T=0)} \int_0^\infty k^4 \exp \left[ -\lambda \frac{\hbar^2 k^2}{2m} \right] dk_{is} \]

\[ = \frac{V \hbar^2}{4m\pi^2} e^{-\mu(T=0) - \lambda E_I} \int_0^\infty k^4 \exp \left[ -\lambda \frac{\hbar^2 k^2}{2m} \right] dk_{is} \]

\[ = \frac{3V}{2\lambda} e^{-\mu(T=0) - \lambda E_I} \left[ \frac{m}{2\pi\hbar^2} \right]^{3/2} \]

\[ = \frac{3V}{2\lambda} e^{-\mu(FDS)} \left[ \frac{m}{2\pi\hbar^2} \right]^{3/2}. \]
FIG. 1: Equation (4) has been employed to fit the experimental $\rho(T)$ plots for Ga$_{1-x}$MnAs as given in a) whereas Eq. (5) is used to fit the plots in b). All fittings are indicated with solid lines. b) is actually for annealed non-ferromagnetic Ga$_{0.930}$Mn$_{0.070}$As samples. c) and d) show the $T$ variation of calculated $M_{x}(T)/M_{0}$ (α = K, TD, $\rho$) with $S = 1$ for $x = 0.060$ and 0.070 respectively. $M_{x}(T)/M_{0}$ is also calculated with $S = 5/2$. The experimental $M_{exp}(T)/M_{0}$ plot for $x = 0.070$ (as grown) is shown in d).

FIG. 2: Experimental plots of $\rho(T)$ for La$_{1-x}$Ca$_{x}$MnO$_{3}$ at $x = 0.1$, 0.2 and 0.2 (6 T) have been fitted with Eq. (6) as depicted in a) and b). All fittings are indicated with solid lines. Whereas c) and d) show the $T$ variation of calculated $M_{x}(T)/M_{0}$ (α = K, TD, $\rho$) with $S = 1$ for $x = 0.1$ and 0.2 respectively. The experimental $M_{exp}(T)/M_{0}$ plot for $x = 0.2$ is given in d).

FIG. 3: a) Equation (7) has been employed to fit the experimental $\rho(T)$ plots for Mn$_{0.02}$Ge$_{0.98}$. The plot with additional constraint, $dM_{x}(T)/dT = 0$ on Eq. (7) is also given to emphasize the influence of $M_{x}(T)/M_{0}$ for an accurate fitting. In these two plots, $A = 25$, $B = 1060$ and $E_{1} + E_{F} = 15$ K. The $T$-dependence of $\rho(T)$ in accordance with $J_{c}$ only, ignoring $J_{c}$ is calculated with Eq. (8), which lacks the ability to capture the experimental $\rho(T, x = 0.02)$. In this case, $A_{0} = 1.8$ and $E_{1} + E_{F} = 15$ K. Both $E_{1} + E_{F} = 15$ K and $E_{1} + E_{F} = 80$ K give $p$ in the order of $10^{19}$ cm$^{-3}$ using Eq. (7) and $m_{e}$ is rest mass. b) Shows the $T$ variation of $M_{x}(T)/M_{0}$ (α = K, TD, $\rho$, exp) for $x = 0.02$. Notice the inequality, $M_{x}(T)/M_{0} > M_{0}$ as $M_{exp}(T)/M_{0}$ that arises as a result of the principle of least action. The $T$-dependence of $M_{x}(T)/M_{0}$ is close to the Ga$_{1-x}$Mn$_{x}$As DMS, rather than the traditional manganites. As such, this behavior is suspected to be associated with the multiple exchange interaction.

### Table I: Calculated values of $T$ independent electron-electron scattering rate constant ($A$), $B$, which is a function of $T$ independent spin disorder scattering rate constant and spin exchange energy ($J_{c}$) as well as the ionization energy ($E_{F}$). All these parameters are for Mn doped Ga$_{1-x}$Mn$_{x}$As (as grown and annealed at 370 °C, 390 °C) and Ca doped La$_{1-x}$Ca$_{x}$MnO$_{3}$ (measured at 0 and 6 T) systems. All Ga$_{1-x}$Mn$_{x}$As samples were measured at 0 T.

| Material | $A$ | $B$ | $J_{c}$ | $E_{F}$ |
|----------|-----|-----|--------|--------|
| Mn doped Ga$_{1-x}$Mn$_{x}$As | | | | |
| As grown | | | | |
| Annealed | | | | |
| La$_{1-x}$Ca$_{x}$MnO$_{3}$ | | | | |
| Measured at 0 T | | | | |
| Measured at 6 T | | | | |

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**Theory**

- \( B_0: x = 0.070 \) (as grown)
- \( A_1: x = 0.060 \) (ann: 370 °C)

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**Experimental data points** were taken from Van Esch et al. [17]

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**Ga\(_{1-x}\)Mn\(_x\)As**

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**Tinbergen-Dekker [19]**

**Kasuya (S=1) [20]**

**Exp. (0.2 mT)**

**1-Mp(T)/Mo**

**Kasuya (S=5/2)**
| Sample                  | Ann. $T(H)$ °C(Tesla) | $A$ [Calc.] | $B$ [Calc.] | $E_I + E_F$ [Calc.] K(meV) | $T_C(T_{cr})$ K [17,18] |
|------------------------|------------------------|-------------|-------------|-----------------------------|--------------------------|
| Ga$_{0.940}$Mn$_{0.060}$As [1] | 370 (0)                | 4.5         | 400         | 8 (0.69)                    | 50 (10)                  |
| Ga$_{0.933}$Mn$_{0.070}$As [1] | As grown (0)           | 9.2         | 400         | 12 (1.04)                   | 45 (12)                  |
| Ga$_{0.930}$Mn$_{0.070}$As [1] | 370 (0)                | 0.02        | ~           | 280 (24.2)                  | ~                        |
| Ga$_{0.930}$Mn$_{0.070}$As [1] | 390 (0)                | 0.03        | ~           | 400 (34.5)                  | ~                        |
| La$_{0.9}$Ca$_{0.1}$MnO$_3$ [2] | ~ (0)                  | 10          | 0.65        | 1400 (121)                  | 222 (~)                  |
| La$_{0.8}$Ca$_{0.2}$MnO$_3$ [2] | ~ (0)                  | 10          | 1.2         | 1300 (112)                  | 246 (~)                  |
| La$_{0.8}$Ca$_{0.2}$MnO$_3$ [2] | ~ (6)                  | 5           | 3.2         | 900 (78)                    | 251 (~)                  |
La$_{1-x}$Ca$_x$MnO$_3$

Experimental data points were taken from Mahendiran et al. [18]

La$_{1-x}$Ca$_x$MnO$_3$

Kasuya (S=1) [20]

1-Mp(T)/Mo
$A_h = 1.8$

$E_1 + E_F = 80 \text{ K}$

Exp. data: [22]

Eq. (7): $dM_p(T)/dT = 0$

Eq. (9)

$\rho(\text{m}\Omega \text{cm})$

$M(\alpha(T))/M_0$: [22]

$M_{ex}(T)/M_0$ [22]

$M_p(T)/M_0$

$M_k(T)/M_0$

Ge$_{0.98}$Mn$_{0.02}$ Park et al. [22]