Universal spin-dependent variable range hopping in wide-band-gap oxide ferromagnetic semiconductors*

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This paper proposes a universal spin-dependent variable range hopping theoretical model to describe various experimental transport phenomena observed in wide-band-gap oxide ferromagnetic semiconductors with high transition metal concentration. The contributions of the 'hard gap' energy, Coulomb interaction, correlation energy, and exchange interaction to the electrical transport are considered in the universal variable range hopping theoretical model. By fitting the temperature and magnetic field dependence of the experimental sheet resistance to the theoretical model, the spin polarization ratio of electrical carriers near the Fermi level and interactions between electrical carriers can be obtained.

Keywords: variable range hopping, ferromagnetic semiconductors, electrical transport, spin polarization

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1. Introduction

Magnetic semiconductors obtained by doping transition metal (TM) elements into host nonmagnetic semiconductors, mostly III–V and II–VI compounds, are key functional materials for spintronics applications. In addition to the intrinsic ferromagnetism, magnetic semiconductors are expected to contain spin-polarized carriers. Hence, much research has been done on the electrical transport and magnetoresistance.[1−16] Recently, wide-band-gap ferromagnetic semiconductor films of ternary oxides with high TM concentration, such as $Zn_{1-x}Co_xO_{1-v}$, $Zn_{1-x}Fe_xO_{1-v}$, $Ti_{1-x}Co_xO_{2-v}$, $(In_{1-x}Fe_x)_2O_{3-v}$, and $(Al_{1-x}Co_x)_2O_{3-v}$ (x means the TM concentration, and v means oxygen vacancy), were prepared under thermal non-equilibrium conditions, and ferromagnetism above room temperature was found.[10−15] Various electrical transport mechanisms have been observed in these materials, such as Mott variable range hopping (VRH) in $(In_{1-x}Fe_x)_2O_{3-v}$,[11] spin-dependent Efros VRH in $Zn_{1-x}Co_xO_{1-v}$ and $Ti_{1-x}Co_xO_{2-v}$,[12] and 'hard gap' resistance in $Zn_{1-x}Fe_xO_{1-v}$ and $(Al_{1-x}Co_x)_2O_{3-v}$.[13,15] Moreover, they show a large spin-dependent magnetoresistance in the variable range hopping region, indicating that not only electron–electron Coulomb interaction but also spin–spin exchange interaction plays a role in the electrical transport. However, a universal relation between the electrical transport mechanisms and various interactions in all these materials has not been obtained and is highly desirable.

In this paper, we propose a spin-dependent VRH theoretical model which takes into account various contributions of the 'hard gap' energy, Coulomb interaction, correlation energy, and exchange interaction to describe observed experimental results. By fitting the temperature and magnetic field dependence of the experimental sheet resistance to the theoretical model, we can obtain the spin polarization ratio of electrical carriers near the Fermi level and interactions between electrical carriers.

2. Experiments

Our theoretical research is based on the understanding of the electrical transport properties of a novel family of wide-band-gap oxide ternary ferromagnetic semiconductors with high TM concentrations. These films have similar nominal structures [TM x

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Å/ oxide y Å]$_z$, which were synthesized by alternatively sputtering very thin (x = 2–6 Å) TM layers and (y = 2–20 Å) oxide layers for z (z = 30–60) periods under precisely controlled mixtures of argon and remnant oxygen atmosphere at room temperature on glass substrates. Due to atomic interdiffusion, we obtain metastable nanocrystalline or amorphous ternary oxides with high TM concentration, which are confirmed by x-ray diffraction and high resolution transmission electron microscopy measurements. The magnetic properties were measured by a superconducting quantum interference device (SQUID), and ferromagnetism above room temperature was observed. The electrical transport measurements were carefully performed on a Van der Pauw configuration by SQUID with applied magnetic field parallel to the film plane.

3. Theoretical electrical transport model

It is found that in the wide-band-gap ferromagnetic semiconductors of ternary oxides with high TM concentration, oxygen vacancies play a key role in ferromagnetic origin and electrical transport. It is commonly believed that 3d states of the TM element are strongly localized (non-conducting) and supply spins (magnetic moments), but the oxygen vacancies are weakly localized and supply carriers (conducting by hopping). The calculation on Fe doped In_2O_3 magnetic semiconductor with oxygen vacancies indicates that the spin of weakly localized s, p carriers of oxygen vacancies (mainly from partial Fe 3d and Fe 4s electrons trapped in oxygen vacancies) are coupled parallel to the minor 3d spin of its nearest localized TM dopant (Fe) due to strong exchange coupling.[17] As a result, the carriers should be polarized and could 'feel' not only the local electrical potential but also the local magnetic potential. Electrical transport is established via spin-dependent VRH between different localized states of oxygen vacancies.[12,13] The spin-dependent VRH resistance of the weakly localized oxygen vacancies is mainly determined by the energy difference ε between the initial occupied i state and the final vacant j state of the hopping process, which is related to the effective interactions between carriers in a magnetic semiconductor system.

According to Viret *et al.*[18] and Ambegaokar *et al.*,[19] we know that $\rho_{ij} \sim \exp(2r/\xi + \varepsilon/k_{\rm B}T)$. Here, ρ_{ij} is the hopping resistance between two localized states i and j at the distance r, $r = |r_i - r_j|$ is the distance between the initial occupied i state and the final vacant j state in real space, ξ is the localization length of the carriers, $k_{\rm B}$ is the Boltzmann constant. In the spirit of work by Inoue and Maekawa[20] and Ju and Li[21], we consider the influence of spin polarization and relative direction of spins on the tunneling probability, and we get $\rho_{ij} \sim 1/(1 + P^2 \cos\theta)$. Here, P is the spin polarization ratio of the carriers near the Fermi level, θ is the angle between the spin S_i in the initial i state and S_j in the final j state of a hopping process. Therefore, the hopping resistance (ρ_{ij}) of the weakly localized oxygen vacancies between two localized states i and j of an energy difference ε can be given as:[12,13]

$$\rho_{ij} = \frac{\rho_0}{1 + P^2 \cos\theta} \exp(2r/\xi + \varepsilon/k_{\rm B}T), \qquad (1)$$

where ρ_0 is a resistance prefactor. In principle, ε includes contributions of all interaction energies of the hopping process, such as Coulomb interaction, correlation energy, 'hard gap' energy, exchange interaction, Zeeman energy, spin–orbit coupling energy and so on. But for a given practical system, it may be that only a few energy terms take a critical role in determining the transport mechanism and the other energy terms can be neglected. We assume that the total energy difference ε between the initial occupied i state and the final vacant j state of a hopping process at the distance r takes the following form:[22,23]

$$\varepsilon = E_{\rm H} + \frac{C}{r^m} - \frac{J\cos\theta}{r^m}. \qquad (2)$$

In Eq. (2), the $E_{\rm H}$ term is a constant 'hard gap' energy,[23–25] the C/r^m term describes the electrical interaction (such as $m = 1$ represents Coulomb interaction, and $m = 3$ represents correlation energy),[22,26,27] the $J\cos\theta/r^m$ term represents magnetic interaction (such as exchange interaction),[28] C and J are two constant coefficients, and m is an integer. Substituting Eq. (2) into Eq. (1), and finding the optimal hopping distance $r = r_{\rm h}$ at a certain temperature T to minimize the hopping resistance ρ_{ij}, we get

$$r_{\rm h} = \left[\frac{m\xi(C - J\cos\theta)}{2k_{\rm B}T}\right]^{1/(m+1)}, \qquad (3)$$

$$\rho_{ij} = \frac{\rho_0}{1 + P^2\cos\theta} \exp\left[\frac{T_{\rm H}}{T} + \left(\frac{T_{\rm M}}{T}\right)^{1/m+1}\right], \qquad (4)$$

where

$$T_{\rm H} = \frac{E_{\rm H}}{k_{\rm B}},$$

and

$$T_{\rm M} = \left(\frac{m+1}{m}\right)^{m+1} \frac{m2^m(C - J\cos\theta)}{k_{\rm B}\xi^m}. \quad (5)$$

In spite of all hopping paths, it is natural to assume that the resistance of the entire system is determined in order of magnitude by the optimal hopping resistance ρ_{ij}.[29] On the other hand, for the entire system, the spins of the localized states may have their own local magnetization easy axes. Supposing that the Hund's coupling is strong, we find that the spin of a weakly localized s or p carrier is coupled to the spin of its nearest local Co atom (along the local easy axis of the magnetization). Therefore, considering all optimal hopping paths in the entire system, the angle θ may have a distribution and varies with the applied magnetic field. As a simple approximation, the hopping resistance of the entire system is obtained by averaging $\cos\theta$ in Eqs. (4) and (5), i.e., ρ can be described as

$$\rho = \frac{\rho_0}{1 + P^2 < \cos\theta >} \times \exp\left[\frac{T_{\rm H}}{T} + \left(\frac{< T_{\rm M} >}{T}\right)^{1/m+1}\right], \quad (6)$$

where

$$< T_{\rm M} >= \left(\frac{m+1}{m}\right)^{m+1} \frac{m2^m(C - J < \cos\theta >)}{k_{\rm B}\xi^m}. \quad (7)$$

In Eqs. (6) and (7), $< \cos\theta >$ represents the average of $\cos\theta$. If we further suppose a random distribution of the easy magnetization axes, we obtain $< \cos\theta >= m^2$, where m stands for the reduced magnetization of the entire system. In particular, $< \cos\theta >= m^2 = 0$ in the demagnetized state (or the as-deposited films without experiencing any magnetic field), while $< \cos\theta >= m^2 = 1$ is in the magnetic saturation state. Since the angle θ varies with applied magnetic field, equation (6) can describe not only the temperature dependence but also the applied magnetic field dependence (magnetoresistance) of the hopping resistance. The above approximation is not strict in mathematics, but it is physically accurate enough for describing all the observed experimental results. It should be pointed out that if only Coulomb interaction and magnetic exchange interaction dominate the electrical transport, i.e., $E_{\rm H} = 0$ and $m = 1$ in Eq. (2), equation (6) is reduced to Yan's previous work.[12] If the 'hard gap' energy, Coulomb interaction and magnetic exchange interaction all play a role in electrical transport, i.e., $E_{\rm H} \neq 0$ and $m = 1$ in Eq. (2), equation (6) is consistent with Tian's previous work.[13]

Although equations (6) and (7) are more universal to describe all the observed experimental results, we can further simplify them to reveal the main interactions and various electrical transport mechanisms. For example, when we discuss the electrical transport results without experiencing any magnetic field, $< \cos\theta >= 0$ is satisfied. According to Eqs. (6) and (7), the exchange interaction term becomes zero, i.e., we do not need to consider the exchange interaction term when we deal with the electrical transport of the as-deposited films without experiencing any magnetic field. In fact, even at the saturation magnetic field, the effects of the magnetic interaction on the hopping resistance are still very small in comparison with the effects of the electrical interaction. When $< \cos\theta >= 0$, the universal description of Eq. (6) can be further reduced into a simple equation, i.e.,

$$\rho = \rho_0 \exp\left[\left(\frac{T_{\rm l}}{T}\right)^n\right], \quad (8)$$

where $T_{\rm l}$ is a coefficient, and different values of $n (n = 1/4, 1/2,$ and $1)$ reveal different electrical transport mechanisms. Three experimental cases are discussed in the following.

(i) Consider the simplest system of oxide magnetic semiconductors, which does not have Coulomb interaction and 'hard gap' energy, i.e., the Mott VRH system.[30] In this case, $E_{\rm H} = 0$, $m = 3$, and $C = \alpha_1/g$, equation (2) becomes Eq. (9), i.e.,

$$\varepsilon = \frac{\alpha_1}{gr^3}, \quad (9)$$

where α_1 is a prefactor of order unity and g is the constant density of states at the Fermi level. The $\varepsilon = \alpha_1/gr^3$ can be regarded as correlation energy in the four-dimensional r–E space (three spacial coordinates and one energy) which should be satisfied for Mott VRH,[22,26] and then equation (6) becomes Mott VRH,

$$\rho = \rho_0 \exp\left[\left(\frac{T_{\rm Mo}}{T}\right)^{1/4}\right], \quad (10)$$

where $T_{\rm Mo} = (4/3)^4 24\alpha_1/(gk_{\rm B}\xi^3)$. This means that equation (10) is one case of Eq. (8) for $n = 1/4$ and $T_{\rm l} = T_{\rm Mo}$.

(ii) The most important interaction that should be considered in a localized system is the Coulomb interaction between the carriers, i.e., $\varepsilon = \alpha_2 e^2/(\kappa r)$,

where α_2 is a prefactor of order unity, e is the electronic charge, and k is the dielectric constant. In this case, equation (2) becomes Eq. (11),

$$\varepsilon = \frac{\alpha_2 e^2}{\kappa r} \tag{11}$$

and equation (6) becomes Efros VRH,[27]

$$\rho = \rho_0 \exp\left[\left(\frac{T_{\rm ES}}{T}\right)^{1/2}\right], \tag{12}$$

where $T_{\rm ES} = 8\alpha_2 e^2/(\kappa k_{\rm B}\xi)$. This means that equation (12) can be regarded as the second case of Eq. (8) for $n = 1/2$ and $T_{\rm l} = T_{\rm ES}$.

(iii) As for the 'hard gap' energy $E_{\rm H}$, it can be considered as a constant in spite of its various magnetic or electrical origins.[23−25] One important case is the many-electron excitation effect[25] induced by a single VRH, which could lead to a 'hard gap' in the density of state near the Fermi level. If the 'hard gap' term $T_{\rm H}/T$ dominates over $(T_{\rm M}/T)^{1/m+1}$ term, equation (6) becomes 'hard gap' transport, i.e.,

$$\rho = \rho_0 \exp\left(\frac{T_{\rm H}}{T}\right). \tag{13}$$

It is clear that equation (13) can be regarded as the third case of Eq. (8) for $n = 1$ and $T_l = T_{\rm H}$.

4. Theoretical fitting to experimental results

In Fig. 1, the temperature dependence of the sheet resistance for $Zn_{0.14}Fe_{0.86}O_{1-v}$ magnetic semiconductors under 0 and 5 T magnetic field is given as an example of the studied oxide ferromagnetic semiconductors with high TM concentrations. In Fig. 1(a), a linear relationship between $\ln\rho$ and T^{-1} is observed in the low temperature range, which means that 'hard gap' energy dominates the electrical transport in the low temperature range. In Fig. 1(b), a linear relationship between $\ln\rho$ and $T^{-1/2}$, i.e., Efros VRH, is observed in the relatively high temperature range, which means that Coulomb interaction dominates the electrical transport at relatively high temperatures. Moreover, the linear relation of $\ln\rho$ versus T^{-1} in Fig. 1(a) (or $T^{-1/2}$ in Fig. 1(b)) is not changed at a saturation magnetic field except that the slopes and intersections are slightly different in comparison with the case without magnetic field. Therefore, in Fig. 1(c), experimental sheet resistance is fitted by Eqs. (6) and (7) with $m = 1$, where 'hard gap' energy, Coulomb interaction, and exchange energy are considered. Good agreement is clearly obtained in a wide temperature range and under different magnetic fields, revealing that our transport model can describe various transport phenomena observed in wide-band-gap oxide ferromagnetic semiconductors. In addition, from the theoretical fitting parameters given in Fig. 1(c), we can derive that the spin polarization ratio of $Zn_{0.14}Co_{0.86}O_{1-v}$ is 30%. The high spin polarization ratio and high Curie temperature (> 100 °C) make the $Zn_{1-x}Fe_xO_{1-v}$ ferromagnetic semiconductor a promising candidate for spintronics.

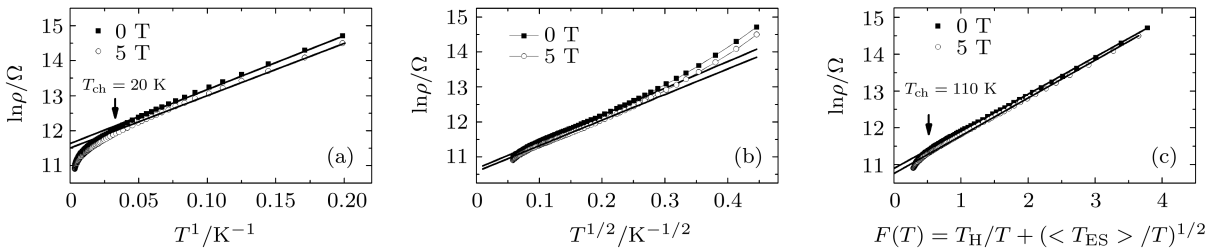


Fig. 1. Sheet resistance in logarithmic scale vs (a) T^{-1}, (b) $T^{-1/2}$, and (c) $F(T) = T_{\rm H}/T + (< T_{\rm M} > /T)^{1/2}$ for $Zn_{0.14}Fe_{0.86}O_{1-v}$ oxide ferromagnetic semiconductor films. Solid straight lines are theoretical results with fitting parameters for (a) $\rho_0 = 1.1280 \times 10^5$ Ω, $T_{\rm H}(0) = 15.6173$ K, $\rho_0(5\ {\rm T}) = 9.9400 \times 10^4$ Ω, $T_{\rm H}(5\ {\rm T}) = 15.1374$ K by Eq. (13); (b) $\rho_0 = 4.2864 \times 10^4$ Ω, $T_{\rm ES}(0) = 58.5493$ K, $\rho_0(5\ {\rm T}) = 3.9656 \times 10^4$ Ω, $T_{\rm ES}(5\ {\rm T}) = 53.4317$ K by Eq. (12); (c) $\rho_0 = 5.3873 \times 10^4$ Ω, $T_{\rm H}(0) = 8.3543$ K, $T_{\rm M}(0) = 23.1016$ K, $\rho_0(5\ {\rm T}) = 4.9412 \times 10^4$ Ω, $T_{\rm H}(5\ {\rm T}) = 8.3543$ K, $T_{\rm M}(5\ {\rm T}) = 20.4798$ K by Eqs. (6) and (7). In Fig. 1, $T_{\rm ch}$ is the temperature from which experimental results deviate from theoretical fittings.

5. Conclusions

In conclusion, we have proposed a universal spin-dependent VRH theoretical model for better understanding of the electrical transport properties with spin-polarized carriers in wide-band-gap oxide ferromagnetic semiconductors under various electrical and magnetic interactions. Good agreement between theoretical fittings and experimental results is obtained. The universal spin-dependent VRH theoretical model should be suitable for other magnetic semiconductor systems with spin-polarized carriers if the 'hard gap' energy, Coulomb interaction, correlation energy, and exchange interaction dominate the electrical transport in these systems.

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