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Correlated Small Polaron Transport in Mixed Valence Oxides

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Abstract : The electrical transport properties of mixed ferrites, oxidic superconductors and GMR compounds having ions in mixed valence state are shown to originate from the correlated motion of polarons and scattering by the spin disorder.

The transport properties of mixed valence compounds exhibit anomalous characteristics. In magnetite, it leads to a order-disorder transition at 120 K with Λ -type anomaly in the specific heat, which is well below the curie temperature, $T_c = 850$ K [1]. In oxidic superconductors, like $(La_{1-x}Sr_x)_2CuO_4$ and $YBa_2Cu_3O_{7-\delta}$, the normal state resistivities show remarkable linear-T metallic behaviour over a wide temperature range [2]. In a negative giant magnetoresistance material like $La_{1-x}Ca_xMnO_3$, a metallic conductivity is observed below the curie temperature and an activated conductivity at $T \geq T_c$ [3]. We show that a possible reason for these anomalies arise from the existence of mixed valence states $A^{\pm m}$, $A^{\pm(m+1)}$ on crystallographic similar sites where A is a cation or an anion.

Based on a concept of short-range cooperative charge transfer between mixed valence states arising from electron-phonon coupling an expression for dc conductivity is obtained [4] :

$$\sigma = (2/\pi) n \omega_{ph} a^2 e^2 \beta \operatorname{sech}^2 (\beta \epsilon_p / 2) \quad (1)$$

where n is the number of ions in the mixed valence state, ω_{ph} is the frequency of the longitudinal optic phonon mode which couples the neighbouring ions separated by a distance a , ϵ_p is the stabilization energy of the small polaron and $\beta = 1/k_B T$.

Equation (1) describes satisfactorily the transport in mixed ferrites [4] as well as in normal state oxidic superconductors [5]. The Verwey transition in magnetite has been attributed to softening of the phonon mode, consequently ω_{ph} in eq.(1) vanishes at $T = T_v$ [6]. In magnetite, the expression in eq.(1) applies only in the temperature range $T_v < T < 250$ K. The reason is that scattering of charges by spin-disorders on the linear chain is totally ignored. To incorporate it, we express the time, τ , between two collisions of the charge carrier in the Drude formula, $\sigma = ne^2 \tau / m^*$, in the form,

$$\frac{1}{\tau} = \frac{1}{\tau_c} + \frac{1}{\tau_s} \quad (2)$$

where τ_c is the collision time obtained from eq.(1) for the correlated motion and τ_s is the time due to spin-flip arising from the exchange interaction. We may describe τ_s quasi-classically as,

$$\frac{1}{\tau_s} = A [1 - m(t)] \langle S_z \rangle \quad (3)$$

Here $m(t)$ is the reduced magnetization at $t = T/T_c$ and $\langle S_z \rangle$ is the average of the z component of the spin of the electron making the jump. To a first approximation, if we take A as $1/\tau_c$, we obtain from eq.'s (1) and (3),

$$\begin{aligned} \sigma(t) &= C \beta \operatorname{sech}^2 (\beta \epsilon_p / 2) [1 - \{1 - m(t)\} \langle S_z \rangle] \\ C &= (2/\pi) n \omega_{ph} a^2 e^2 \end{aligned} \quad (4)$$

This expression fits the experimental data of Miles et al. [7] for magnetite over the temperature-range $T_v \leq T \leq T_c$ if we take $\langle S_z \rangle \approx 2m(t)$ for Fe^{2+} minority spin carriers [Fig. 1].

In GMR compounds like $La_{1-x}Ca_xMnO_3$, the resistivity at $T = 0$ tends to zero and it also decreases for $T \gg T_c$. So a maximum occurs near T_c [3]. On application of an external magnetic field the magnetoresistance, $\Delta\rho(H) = \rho(H) - \rho(0)$ in the system $La_{1-x}Ca_xMnO_3$ [$0.1 \leq x \leq 0.9$], is observed to be negative. $LaMnO_3$ is a weak ferromagnet and an insulator. When Ca^{2+} ions are substituted for La^{3+} , the d-holes move amongst the equivalent Mn positions. However, for small hole concentrations,

correlated polaron motion is not possible and the transport is described by the independent polaron motion. In this case, the Frank-Condon factor, $\exp(-E_p/\omega_{ph})$, where E_p is the polaron binding energy and ω_{ph} is the phonon frequency, appears in the expression for conductivity [8] and explains the maximum in the resistivity versus temperature curve. The scattering of the holes is dominated by the spin-flip term and the magnetoresistance is given by,

$$\frac{\rho(H) - \rho(0)}{\rho(0)} = -m(H, t) \langle S_z(H) \rangle \quad (5)$$

where the quantities on the right indicate the values based on short range ordering of the spin systems. Equation (5) explains the negative magnetoresistance of the system.

We conclude that the electrical transport properties in mixed valence compounds can be explained satisfactorily on the basis of correlated polaron and spin flip scattering processes.

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Fig.(1) Conductivity vs temperature for Fe_3O_4 . Experimental points (o) are from ref.[7]. The theoretical curve (solid line) is from eq.(4) [see text].