Low-temperature electrical transport and double exchange in 

$\text{La}_{0.67}(\text{Pb,Ca})_{0.33}\text{MnO}_3$.

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Abstract

The resistivity in the ferromagnetic state of flux-grown $\text{La}_{2/3}(\text{Pb,Ca})_{1/3}\text{MnO}_3$ single crystals, measured in magnetic fields up to 7 T, reveals a strong quadratic temperature dependence at and above 50 K. At lower temperatures, this contribution drops precipitously leaving the resistivity essentially temperature independent below 20 K. The Seebeck coefficient also reflects a change of behavior at the same temperature. We attribute this behavior to a cut-off of single magnon scattering processes at long wavelengths due to the polarized bands of a double-exchange ferromagnet.

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The substitution of divalent A-atoms in such manganites as La$_{1-x}$A$_x$MnO$_3$ has long been known to induce ferromagnetism and anomalous transport properties, yet an understanding of the underlying mechanisms remains incomplete. The double exchange mechanism, first proposed by Zener [2] and later developed by Anderson and Hasegawa [3], by Kubo and Ohata (KO) [4] and by Furukawa [5], is generally agreed to provide a description of the ferromagnetic ground state. In that model, strong Hund’s Rule coupling enhances the hopping of $e_g$ electrons between neighboring Mn$^{3+}$ and Mn$^{4+}$ ions by a factor $\cos(\theta_{ij}/2)$, where $\theta_{ij}$ is the angle between the spin of their respective $t_g$ cores, thereby producing a ferromagnetic interaction. The onset of ferromagnetic order either shrinks the minority-spin bandwidth to zero as the majority bandwidth grows (KO picture) or shifts spectral weight from minority- to majority-band without a change in bandwidth or position (Furukawa picture). Both are distinct from the usual intinerant ferromagnetic scenario in which there is simply a rigid energy displacement of majority and minority bands. It has been argued [6] that electron-phonon coupling is important, but we assume that those effects dominate near and above the ferromagnetic transition which is not our focus here.

In the KO picture, the minority band narrows at absolute zero to a resonance at the band center, resulting in an energy gap $\mu$ between the majority Fermi level and the lowest accessible minority-spin state. Because single spin-wave scattering requires a spin flip, KO argue that the characteristic $T^2$ temperature dependence of the resistivity of metallic ferromagnets will be suppressed by a factor $\exp(-\mu/k_B T)$. Extending the standard perturbation calculation of Mannari [7] to consider two-magnon processes, they predict a leading $T^{9/2}$ temperature dependence in the resistivity. However, a $T^2$ dependence of the resistivity of manganites is typically observed and has been attributed to electron-electron scattering. [8,9] In this paper we present new resistivity data on single crystals, and demonstrate that the quadratic temperature dependence is strongly suppressed as the temperature is reduced, becoming undetectable below 10 K. We argue that this contribution is due to single-magnon processes and that our results support the gradual development of a half-metallic state. However, the disappearance of minority spin states at the Fermi energy appears to be less
abrupt than in the KO model, favoring instead Furukawa’s, in which the minority-spin states reappear at the Fermi surface as soon as the magnetization decreases from its fully ordered value. Band structure calculations also indicate that minority spin states persist at $E_F$, even at $T = 0$ K. To explore the magnon cut-off, we have extended Mannari’s model to a situation in which a minimum magnon energy is required to induce spin-flip transitions. This is essentially the argument leading to the suppression factor predicted by Kubo and Ohata.

High quality single crystals of nominal composition $\text{La}_{0.66}(\text{Pb}_{0.67}\text{Ca}_{0.33})_{0.34}\text{MnO}_3$, determined by inductively coupled plasma spectroscopy on samples from the same batch, were grown from a 50/50 PbF$_2$/PbO flux. Samples grown without Ca in the flux exhibited low Curie temperatures, indicating poor sample quality and/or deviations from optimal doping. Specimens were cut along crystalline axes from larger pre-oriented crystals. X-ray diffractometry shows a single pseudo-orthorhombic structure with lattice parameters $a = 5.472(4)$ Å, $b = 5.526(6)$ Å, and $c = 7.794(8)$ Å. Gold pads were evaporated onto both oriented and unoriented crystals using both standard four-terminal and Montgomery eight-corner contact arrangements. Electrical contact was made with Au leads attached with silver paint. After a 2-hour anneal at $300^\circ C$, contact resistances $< 1$ Ω were achieved. The Seebeck coefficient was measured using a variation of the two-heater method described by Resel, et al.; Chromel and Constantan wires, calibrated against a YBa$_2$Cu$_3$O$_7$ superconducting sample, permitted this method to be used up to 80 K. The resistivity was measured from 2 K to 400 K using either a standard four-terminal dc method, or a dc resistance bridge in a Quantum Design PPMS system. Magnetization data on the same crystals were obtained using a Quantum Design MPMS magnetometer.

Figure 1 shows the resistivity of sample sc3, a single crystal of dimensions $1.04 \times 1.24 \times 0.3$ mm$^3$ with $T_C = 300$ K, vs the square of the temperature in fields up to 70 kOe. The data show a dominant $T^2$ temperature dependence with evidence of a small $T^5$ contribution ($10 \mu\Omega$ cm at 100 K). A calculation of the $T^{9/2}$ contribution predicted by KO for two-magnon processes predicts only $0.5 \mu\Omega$ cm at 100 K with appropriate parameters. It is likely, then,
that this is the usual $T^5$ contribution from electron-phonon processes. The inset to Fig. 2 shows that the data do not follow a $T^2$ dependence to the lowest temperatures. Rather, they deviate gradually from the curve $\rho_0 + \alpha(H)T^2$, fit over the range $60 \leq T \leq 160$ K, saturating at an experimental residual resistivity $\rho_{0}^{\exp} = 91.4$ $\mu$Ω cm, comparable to values observed by Urushiba et al. [8], but $\sim 7\%$ larger than $\rho_0$ (see Table I). This conclusion is not changed by including the $T^5$ contribution. Fits to data taken in various fields show that $\alpha_H$ decreases with increasing field and is the source of the small negative magnetoresistance at low temperatures. To quantify the disappearance of the $T^2$ contribution, we numerically differentiate the data, plotting $\alpha(H)^{-1}d\rho/d(T^2)$ in Fig. 2. We have not subtracted the $T^5$ contribution which gives a slight upward curvature to the data at higher temperatures.

Previous investigators have attributed the $T^2$ term in the resistivity to electron-electron scattering, as expected for conventional Fermi liquids. The relaxation rate, however, is then of order $(k_B T)^2/\hbar E_F$. [13] With an electron density of $5.7 \times 10^{27}$ m$^{-3}$ (1/3 doping) and an effective mass ratio $m^*/m = 2.5$ [14] we find $E_F \simeq 0.5$ eV and the $e-e$ relaxation rate of order $2 \times 10^{11}$ s$^{-1}$ at 100 K. The observed $T^2$ contribution at that temperature (cf. Table I) is $100$ $\mu$Ω cm which with the same parameters corresponds to a relaxation rate of $6 \times 10^{13}$ s$^{-1}$, more than two orders of magnitude larger. Rather than vanishing, what is more, $e-e$ scattering should become more apparent as the temperature is reduced. We conclude that $e-e$ scattering is an unlikely explanation for the observed quadratic dependence on temperature.

To test whether single-magnon scattering provides a viable mechanism, we have extended the usual calculation of the electron-magnon resistivity [7] to allow the minority-spin sub-band to be shifted upward in energy such that its Fermi momentum differs by an amount $q_{min}$ from that of the majority sub-band. This should be a reasonable approximation in the intermediate temperature regime in which both minority and majority bands have substantial densities of states at $E_F$. The one-magnon contribution can then be written as

$$\rho_e(T) = \alpha_e T^2,$$
\[ \alpha_\epsilon = \frac{9\pi^3 N^2 J^2 \hbar^5}{8e^2 E_F^4 k_F} \left( \frac{k_B}{m^* D} \right)^2 I(\epsilon). \]  

(1)

In this equation, \( NJ \) is the electron-magnon coupling energy which is large and equal to \( \mu = W - E_F \) in the double-exchange Hamiltonian of KO; \( 2W \) is the bandwidth. The magnon energy is given by \( Dq^2 \), and we have defined

\[ I(\epsilon) = \int_{\epsilon}^{\infty} \frac{x^2}{\sinh^2 x} dx. \]  

(2)

The lower limit is \( \epsilon = Dq_{\text{min}}^2/2k_BT \), where \( Dq_{\text{min}}^2 \) is the minimum magnon energy that connects up- and down-spin bands; this result reproduces Mannari’s calculation in the limit \( \epsilon \to 0 \), and KO’s exponential cut-off for large \( \epsilon \). Within the spin-wave approximation, the low temperature magnetization is given by \( M(T) = M(0) - BT^{3/2} - \ldots \), where \( B = 0.0587 g\mu_B (k_B/D)^{3/2} \). The stiffness constant \( D \) has been determined by neutron scattering \[15,16\] and muon spin resonance \[17\] to be \( D \approx 135 - 170 \text{ meV } \AA^2 \). The inset to Fig. 1 shows the magnetization for this sample, from which we extract \( B(10 \text{ kOe}) \) (Table I) and the value \( D = 165 \text{ meV } \AA^2 \), in good agreement with other results. The effect of an applied field is to open a gap \( \Delta = g\mu_B H \) in the magnon spectrum, resulting in a field-dependent coefficient \( B(H) \approx B(0)(1 - 1.36 \sqrt{\Delta/k_BT} + \ldots) \). The same gap enters the hyperbolic function in Eq.(2), with the result that \( \delta \alpha \equiv \alpha_0(0) - \alpha_0(H) \propto \Delta/k_BT \). Using our high-temperature \( (\epsilon \approx 0) \) fits, we plot \( B(H) \) vs \( \sqrt{\delta \alpha} \) in Fig. 3; that these are proportional supports our assertion that the \( T^2 \) contribution is due to single-magnon scattering. The zero-field intercept corresponds to \( D = 140 \text{ meV } \AA^2 \), reasonably close to the value reported by Perring, et al. for Pb-doped samples. \[18\]

The Seebeck coefficient \( S(T) \) provides additional information on the nature of transport at low temperatures. Fig. 4 shows \( S(T) \), measured on the same sample at \( H = 0 \) and 80 kOe. At the lowest temperatures, \( S(T) \) is positive, linear in temperature, and extrapolates to zero as \( T \to 0 \). The field dependence is small and negative. The large slope suggests, from the Mott formula, that the resistivity is a strong function of energy at \( E_F \). There is a sharp deviation from linear behavior in the temperature range in which the \( T^2 \)-dependence
of the resistivity becomes dominant and the field dependence changes sign and becomes larger. This presumably arises from the onset of magnon scattering which, being a spin flip process, must involve the minority spin band, and which therefore has a different dependence on energy near $E_F$. We note that the peak in the low temperature thermopower that is regularly seen in thin-film samples [19] is absent here, and is therefore not intrinsic to these materials.

At high temperatures, the lower limit of the integral in Eq. (1) can be set equal to zero, leaving only the coupling energy $NJ = W - E_F$ as a parameter. Equating the calculated value to the experimental $\alpha$ from Table I fixes the coupling to be $W - E_F \approx 1.0$ eV or $W \approx 1.5$ eV, in good agreement with a virtual crystal estimate of the band width. [20] In Fig. 2 we have plotted $\alpha_0^{-1}d(\alpha_0 T^2)/d(T^2)$ assuming $D(0)q_{\text{min}}^2 = 4$ meV and including the temperature dependence observed experimentally, $D(T)/D(0) = (1 - T/T_C)^{0.38}$ [16] which is important only at higher temperatures. While the curve follows the data qualitatively, it is clear that the minimum magnon energy is substantially larger than 4 meV at low temperatures, and decreases rapidly with increasing temperature. We note that the leading correction to a $T^2$ dependence from Eq.(1) is negative and linear in $T$, as observed elsewhere. [21]

Clearly, our extension of the magnon resistivity calculation to spin-split parabolic bands greatly oversimplifies the changes in the minority-spin band that accompany magnetic ordering. As a consequence, our calculation cannot be expected to represent accurately the cut-off of magnon scattering due to loss of minority-spin phase space. Nonetheless, the rapid suppression of the $T^2$ contribution to the resistivity and the agreement between its magnitude at higher temperatures with parameters expected for the manganites confirm the basic picture. In the intermediate temperature regime, $0.2 \leq T/T_C \leq 0.5$ here, the manganites appear to be normal metallic ferromagnets with the resistivity dominated by spin-wave scattering. At lower temperatures, the increasingly half-metallic character of the material is manifested by a temperature dependent cut-off of the spin-wave scattering process, leaving in its wake only residual resistivity from the intrinsic doped-in disorder and indistinguishable phonon
and two-magnon contributions. As these heavily doped materials have significant disorder and large residual resistivities we recall that strongly disordered materials also exhibit \( T^2 \) regimes below half the Debye temperature. \[22\] This result, however, an extension of the Ziman theory of liquid metals, sets an upper limit of \( \alpha T^2 / \rho_0 \simeq 0.03 \) before the resistivity changes to a linear temperature dependence; our ratio is unity at 100 K with no evidence for a linear regime. We conclude that the quadratic temperature dependence is not due to phonon scattering in a strongly disordered material.

In summary, our low temperature resistivity data on well-characterized single crystal samples exhibit a dominant \( T^2 \) temperature dependence above 50 K that vanishes abruptly at lower temperatures and is consistent in magnitude and magnetic field dependence with one-magnon scattering processes. Our data cannot be explained by electron-electron scattering as proposed in previous reports. \[19,8,9\] While oversimplified, our extension of the standard calculation of one-magnon resistivity to account for spin-split bands gives a qualitative account of the half-metallic suppression of spin-wave scattering at low temperatures. The onset of significant magnon-mediated scattering near 30 K is also reflected in a change in both the temperature and field dependence of the thermopower. While two-magnon processes may contribute, these are expected to be very small, and cannot be separated from ordinary phonon scattering nor from the rapid increase in resistance that occurs near the Curie temperature. Our data demonstrate that the half-metallic ground state of the doped manganites quickly evolves with increasing temperature into a more conventional, metallic ferromagnet.

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REFERENCES

[1] G.H. Jonker and J.H. Van Santen, Physica 16, 337 (1950); J. Volger, Physica XX, 49 (1954).

[2] C. Zener, Phys. Rev., 82, 403 (1951).

[3] P.W. Anderson and H. Hasegawa, Phys. Rev. 100, 675 (1955).

[4] K. Kubo and N. Ohata, J. Phys. Soc. Jpn. 33, 21, (1972).

[5] N. Furukawa, J. Phys. Soc. Jpn. 64, 3164 (1995); ibid. 2734, (1995); ibid. 63, 3214 (1994).

[6] A.J. Millis, P.B. Littlewood, and B. Shraiman, Phys. Rev. Lett. 74, 5144 (1995).

[7] I. Mannari, Prog. Theor. Phys. Jpn. 22, 335 (1959).

[8] A. Urushibara et al., Phys. Rev. B 51, 14103 (1995). Also S.E. Lofland et al., Phys. Rev. B 52, 15058 (1995).

[9] P. Schiffer et al., Phys. Rev. Lett. 75, 3336 (1995). Also G.J. Snyder et al., Phys. Rev. B 53, 14434 (1996).

[10] W. E. Pickett and D. J. Singh, Phys. Rev. B 53, 1146 (1996); D. J. Singh and W. E. Pickett (to be published).

[11] P.D. Han and D.A. Payne, J. Mater. Res. (submitted).

[12] R. Resel et al. Rev. Sci. Inst. 67, 1970 (1996).

[13] N. Ashcroft and D. Mermin, Solid State Physics (Holt, Rinehart, and Winston, New York, 1976) p. 348

[14] J.J. Hamilton et al. Phys. Rev. B 54, 14926 (1996).

[15] J.W. Lynn et al., Phys. Rev. Lett.76, 4046 (1996).
[16] J. Fernandez-Baca et al., (preprint, 1997).

[17] R.H. Heffner et al., Phys. Rev. Lett., 77, 1869 (1996).

[18] T.G. Perring et al., Phys. Rev. Lett. 77, 711 (1996).

[19] M. Jaime et al., Appl. Phys. Lett. 68, 1576 (1996); M. Jaime et al., Phys. Rev. B 54, 11914 (1996); M.F. Hundley and J.J. Neumeier, Phys. Rev. B 55, 11511 (1997).

[20] W. E. Pickett and D. J. Singh, Phys. Rev. B 55, R8642 (1997).

[21] S.E. Lofland, et al. Phys. Rev. B 52, 15 058 (1995).

[22] S. R. Nagel, Phys. Rev. B 16, 1694 (1977).
| La$_{2/3}$A$_{1/3}$MnO$_3$ | $\rho_0$ | $\alpha(H)$ | $B(H)$ | $l_{\text{mag}}^{77K}$ |
|------------------------|---------|-------------|-------|------------------|
|                        | $\mu\Omega$ cm | $n\Omega$ cm K$^{-2}$ | Gauss K$^{-3/2}$ | $\AA$ |
| A = Ca, Pb             |         |             |       |                  |
| sample La5             |         |             |       |                  |
| H = 0                  | 133.33  | 12.79       | -     | 53              |
| 10 kG                  |         |             | 0.014 |                  |
| A = Ca, Pb             |         |             |       |                  |
| sample SC3             |         |             |       |                  |
| H = 0                  | 85.0    | 9.90        | -     | 76              |
| 10 kG                  | 86.8    | 9.73        | 0.0132| 76              |
| 30 kG                  | 86.8    | 9.68        | 0.0125| 77              |
| 50 kG                  | 85.1    | 9.57        | 0.0113| 79              |
| 70 kG                  | 86.2    | 9.46        | 0.0109| 78              |

**TABLE I.** Fitting parameters for resistivity and magnetization as described in the text. The mean free path from electron magnon scattering at 77 K has been calculated.
FIGURES

FIG. 1. The resistivity vs $T^2$ for magnetic fields up to 70 kG in sample sc3. Inset: The difference between the magnetization and its zero-temperature extrapolation vs temperature on a log-log plot, showing $T^{3/2}$ and $T^{5/2}$ contributions.

FIG. 2. The numerical derivative of the data, $\alpha(H)^{-1}d\rho/d(T^2)$, for zero field (■) and 70 kG (□). The dashed curve is the same quantity calculated for the magnon model with $Dq_{\text{min}}^2/k_B = 44$ K. Inset: raw data minus calculated residual resistivity (■) and least-squares curve (dotted line) vs temperature. Note the violation of Matthiessen’s rule at low temperatures.

FIG. 3. The magnetization coefficient $B$ vs the resistivity coefficient $[\alpha(H = 0) - \alpha(H)]^{1/2}$ for four different fields. Proportionality is expected if the $T^2$ temperature dependence is due to one-magnon processes. The line is a linear fit to the data.

FIG. 4. The Seebeck coefficient $S$ vs temperature. It is positive and metal-like at low temperature, has an anomalous kink near 30 K, and develops a positive field dependence above 40 K. The dashed line is a linear fit in the low temperature regime.
\[ \rho (\mu \Omega \text{cm}) \]

\[ T^2 (10^4 \text{ K}^2) \]

\[ H = 0 \]
\[ H = 10 \text{ kG} \]
\[ H = 30 \text{ kG} \]
\[ H = 50 \text{ kG} \]
\[ H = 70 \text{ kG} \]

Figure 1
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