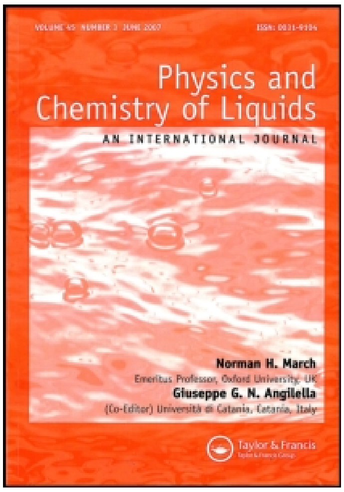

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article March, N. H.(1993) 'Electron or Hole Liquids Flowing Through Antiferromagnetic Assemblies: Relevance to High *T_c* Materials', Physics and Chemistry of Liquids, 25: 2, 65 — 73
To link to this Article: DOI: 10.1080/00319109308030347
URL: http://dx.doi.org/10.1080/00319109308030347

Phys. Chem. Liq., 1993, Vol. 25, pp. 65–73
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REVIEW

Electron or Hole Liquids Flowing Through Antiferromagnetic Assemblies: Relevance to High T_c Materials

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(Received 7 April 1992)

The effects of electron or hole liquids flowing through antiferromagnetic assemblies were discussed in early work by de Gennes. After a brief survey of his main conclusions, attention will be focused on the way such mobile carriers influence the magnetic properties of high T_c cuprates. The effective interaction J between localized Cu spins becomes a function of carrier concentration, p say, while the effective ionic magnetic moment becomes also dependent on p. Other recent work in which both itinerant and bound dopants have been studied are related to de Gennes findings. Finally, some comments are made on Fermi surface and transport properties in relation to certain theoretical models.

KEY WORDS: Exchange coupling, electron or hole dopants, magnetic susceptibility, transport

1 BACKGROUND

Though the motivation for this brief review is afforded by the great interest in high T_c materials following the discovery by Bednorz and Müller[1], it is relevant to note that, as early as 1960, de Gennes[2] discussed some effects associated with mobile carriers in various antiferromagnetic lattices.

His interest then[2] was in magnetic compounds of mixed valency; the example he focused on being $(La_{1-x}Ca_x)(Mn^{3+}_{1-x}Mn^{4+}_x)O_3$. At both ends of the composition diagram, these manganites behave like antiferromagnetic insulators[3,4]. However, if one substitutes 10% of calcium in pure $LaMnO_3$, the room temperature conductivity is increased by two orders of magnitude[3]. The conclusion to be drawn is that the 10% extra holes that have been added are relatively free to move from one manganese ion to another and are able to carry a current. This hole liquid also has a pronounced effect on the magnetic properties of the material: at low temperatures there is a non-zero spontaneous magnetization indicating that some ferromagnetic coupling is present in this case. de Gennes[2] appealed to the earlier work of Zener[5] for the explanation of this fact. Zener's interpretation was that:

i) intra-atomic exchange is strong so that the only important configurations are those where the spin of each carrier is parallel to the local ionic spin

ii) the carriers do not change their spin orientation when flowing through the lattice: accordingly they can hop from one ion to the next only if the two ionic spins are not antiparallel

iii) when hopping is allowed, the ground-state energy is lowered (because the carriers are then able to take part in the binding). This results in a lower energy for ferromagnetic configurations.

This 'double exchange' is, in principle, different from direct or indirect exchange couplings as customarily understood, as emphasized especially by Anderson and Hasegawa[6]. The coupling energy is shared between the carriers and cannot be written as a sum of terms relating the ionic spins by pairs.

de Gennes[2] then shows:

a) There is a pronounced dependence of the carrier energy on the angle between different ionic spins

b) If the pure material is antiferromagnetic, it turns out that the carrier energy in the mixed material is lowered if the sublattices become canted. The energy gain is first order with respect to the angle of canting, while the loss of antiferromagnetic exchange energy is only of second order: this results in the stable arrangement being canted

c) The main macroscopic magnetic predictions, while following from the 'electron or hole liquid' model, remain true for carriers that are bound or nearly bound. The likely relevance of this prediction (c) to the high T_c materials will be taken up again in Section 2.1 below.

2 MAGNETISM OF HIGH T_c MATERIALS

With the above as historical background, let us turn immediately to summarize experimental findings on the way the powder magnetic susceptibility $\chi(T)$ of the high T_c material $La_{2-x}Sr_xCuO_{4-y}$scales with doped hole concentration $p = x - 2y$. The discussion below is based on the work of Johnston[7]. We shall see that the theoretical work of Stechel and Jennison[8] provides a useful framework within which the conclusions of Johnston can be incorporated.

It is worth noting that Johnston's work was carried out against a background in which evidence was accumulating that superconductivity in the high T_c copper oxides develops in the presence of dynamic two-dimensional short-range antiferromagnetic ordering of the Cu spin sublattice. This has, naturally enough, implications for the superconducting mechanism. Johnston's work demonstrated that the magnetic susceptibility χ scales with the doped hole liquid concentration $p = x - 2y$ according to a law of corresponding states for $0 \leq p \leq 0.20$. This then permitted the Pauli susceptibility $\chi^{\mathrm{Pauli}}(p)$ of the hole liquid and the two-dimensional Cu spin sublattice susceptibility, $\chi^{2d}(p, T)$ say, to be separated out and quantitatively estimated. Johnston found that the shape of $\chi^{2d}(T)$ is that of the spin-$\frac{1}{2}$ square-lattice Heisenberg antiferromagnet. However, for a doping concentration p of 0.20, the in-plane Cu–Cu superexchange coupling constant and the effective magnetic moment per Cu ion are both largely suppressed.

Specifically, Johnston noted the following scaling of $\chi(T)$ with p:

$$\chi(p, T) = \chi_o(p) + [\chi_{\mathrm{max}}(p) - \chi_o(p)]\ F(T/T^{\mathrm{max}}(p)), \tag{1}$$

$\chi_o(p)$ being independent of temperature T while $F(z)$ is a universal function. The T dependence of χ is thereby attributed to the effective susceptibility $\chi^{2d}(p, T)$ of the Cu spin sublattice. Johnston gives the scaling quantities $T^{\mathrm{max}}(p)$ and $\chi_{\mathrm{max}}(p)$ as determined from nonlinear regression analyses: this procedure also gave $\chi_o(p)$ to within a constant additive factor. This latter contribution was taken to have the form

$$\chi_0(p) = \chi^{\mathrm{core}} + \chi^{VV} + \chi^{\mathrm{Pauli}}(p), \tag{2}$$

Johnston adopted the following values: $\chi^{\mathrm{core}} = -9.9 \times 10^{-5}$ cm^3/mol, while a powder average of the anistropic T-independent Van Vleck tern was taken to be $\chi^{\mathrm{VV}} = +2.4 \times 10^{-5}$ cm^3/mol. Both χ^{core} and χ^{VV} were taken to be independent of composition over the limited x and y ranges that Johnston was concerned with. Assuming that χ^{Pauli} $(0) = 0$ fixes the additive constant referred to above. Possible contributions to χ from Landau diamagnetism were absorbed into χ^{Pauli}. The scaled Cu sublattice susceptibility thereby extracted by Johnston[7] is reproduced in Figure 1, where the results are compared with various theoretical models. This data turns out to be consistent with a picture in which localized spins are present on the Cu ions in $La_{2-x}Sr_xCuO_{4-y}$ and exhibit dynamic Heisenberg antiferromagnetic intralayer order throughout the metallic as well as the insulating composition regimes. We stress again that Johnston's finding that the magnetic behaviour of the hole liquid and of the Cu spin layers can be separated in this strongly interacting many-body system was anticipated theoretically by Stechel and Jennison[8]. The hole liquid, as already mentioned, does have two important effects on the Cu sublattice magnetism. First, it strongly reduces the effective intralayer Cu–Cu superexchange coupling constant J and secondly the effective magnetic moment per Cu ion is also reduced. Theoretically, for the spin-$\frac{1}{2}$ square lattice Heisenberg antiferromagnet, $J = T^{\mathrm{max}}/1.86$. Using this result, Johnston[7] computed the coupling parameter $J = J(p)$ and his results are reproduced in Figure 2. In keeping with earlier findings noted by Johnston, J decreases rapidly with increasing p. This result is also substantiated by inelastic neutron scattering experiments on single crystals of $La_{2-x}Ba_xCuO_{4-y}$, which reveal that the spin-wave velocity decreases appreciably[7] with increasing p. Also plotted in Figure 2 is $T_c(p)$ as determined by Torrance *et al.*[9] An analysis of the form of this curve has been given in Ref 10; it is suggested there that at low hole concentrations and also at the lowest temperatures, Wigner hole crystallization will occur due to strong hole–hole repulsion.

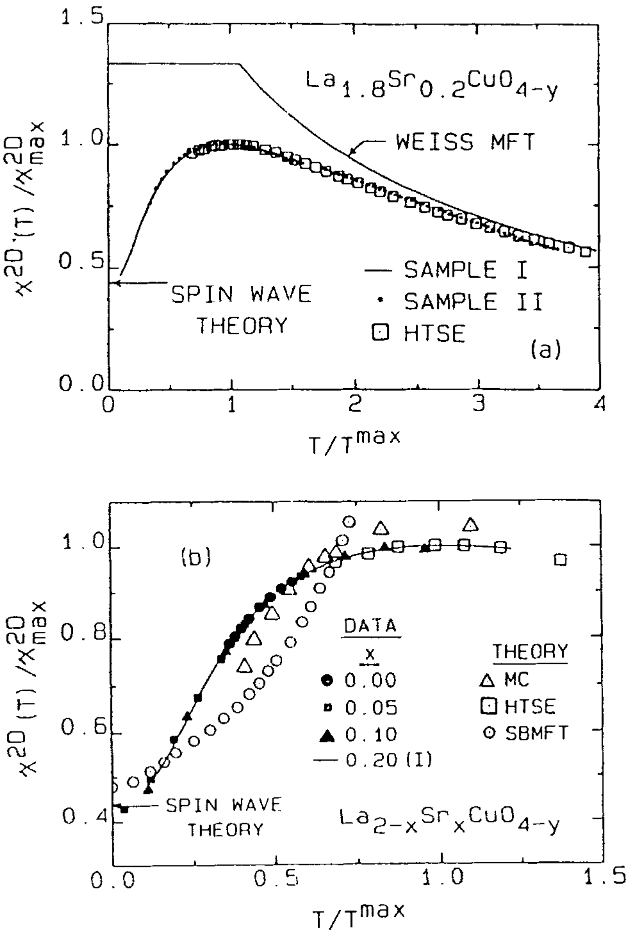

Figure 1 Cu sublattice scaled susceptibility. Extracted susceptibility after removal of Pauli susceptibility of hole liquid is compared with various theoretical predictions (after Johnston[7]).

Having discussed both the magnetic properties of the hole liquid and of the Cu sublattice in $La_{2-x}Sr_xCuO_{4-y}$, we shall briefly summarize some very recent experiments on magnetic properties of another class of high T_c materials in which both electron, and also hole, liquids are present. These findings, it will be suggested below, relate to the predictions of de Gennes summarized in Section 1.

2.1 *Magnetism of* $Bi_2Sr_2Ca_{1-x}M_xCu_2O_8$ with $M = Y$, Gd and Pr

As this article was nearing completion, the work of Gao *et al.*[11] appeared. These workers measured the temperature dependence of (i) magnetic susceptibility, (ii) electrical resistivity and (iii) specific heat in the above material for concentrations $0 < x < 1.0$ and temperatures 1.6 K < T < 300 K. Their findings show that all three dopants, which substitute a trivalent ion for divalent Ca, cause a depression of T_c

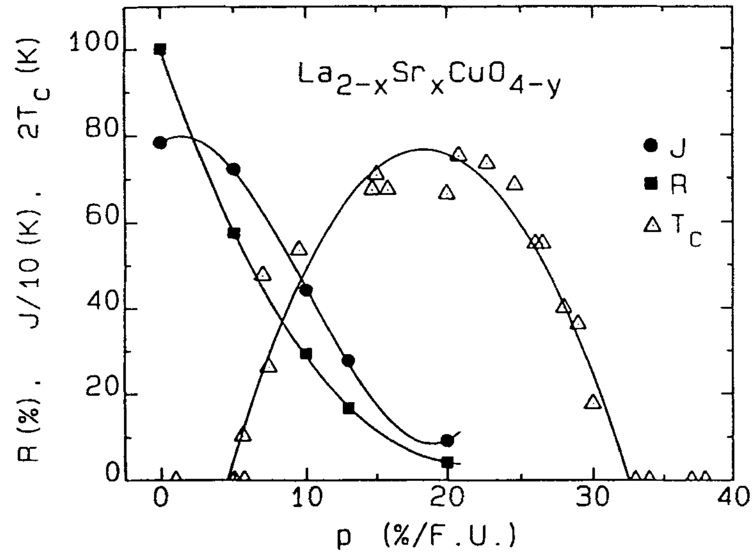

Figure 2 Shows effective $J = J(p)$ as reduced by presence of hole liquid of concentration p. Also shown is $T_c(p)$, from Ref. 9 (Figure taken from Johnston[7]).

observable in the magnetic susceptibility and the resistivity. Both Pr and Gd retain their free-ion magnetic moment and appear to cause insignificant magnetic pair breaking. Their conclusion is that the dominant suppression mechanism in all three cases is driven by the filling of the Cu 3d hole by the extra electron and the breaking of the Cu 3d-O 2*p* hybridization. The localization of Cu 3d holes causes an observable antiferromagnetic ordering of Cu ions within the planes in the case of *Y*. The evidence for Cu ordering for Gd and Pr may be obscured by the large Curie-like contribution to the magnetic susceptibility due to the rare-earth ions.

As Gao *et al.* stress[11], doping studies of $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) provide a very favourable medium for study*. In particular all copper sites are equivalent, the material is easy to make etc.

3 TRANSPORT PROPERTIES OF ELECTRON OR HOLE LIQUIDS

Let us now turn to briefly summarize the experimental findings on the transport properties associated with the electron or hole liquids flowing through specific high T_c materials.

The temperature dependence of the in-plane resistivity of several families of oxide superconductors[12] is shown in Figure 3. Worthy of note is the fact that the resistivities are all about the same in magnitude. Also they increase linearly with temperature over a wide range.

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* It is relevant to note that one of the remarkable findings of de Gennes original study[2], much average behaviour remains the same whether the carriers are nearly free or nearly bound. In this same context, see also Keimer *et al.* (*Phys. Rev.* **B45**, 7430, 1992).

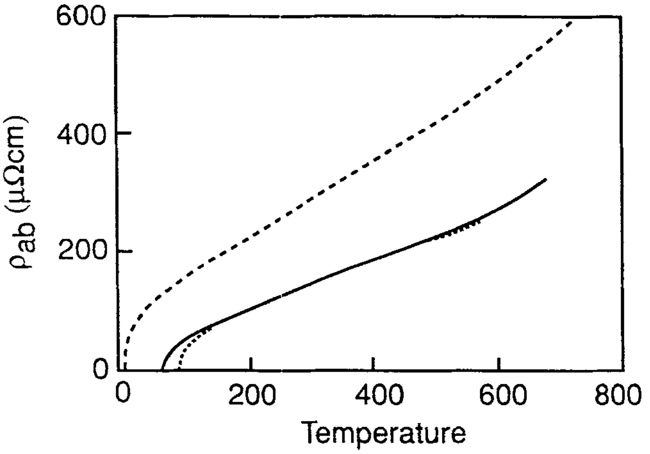

Figure 3 Resistivity as a function of temperature for a family of oxide superconductors. (After Yu Lu[12]).

The behaviour of the Hall constant R_H is shown in Figure 4 where, following Ong[13] the measured values of R_H for the cuprates are compared with conventional Cu metal. Without exploring the detail here, it seems from cursory inspection that the various curves might scale on to each other, especially if it is subsequently found that the curves labelled 123 and 214 have maxima outside the range of the present plots. A model, the so-called three band t–J model, has been analyzed by Haga[14], and it seems possible to understand the main features of the Hall measurements, at least in their qualitative features.

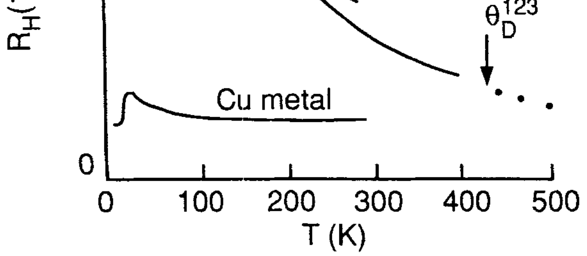

Figure 4 Schematic form of Hall constant R_H for high T_c materials (after Ong[13]), compared with that of Cu metal.

4 SOME THEORETICAL MODELS IN RELATION TO EXPERIMENT

The 3-band t–J model has been referred to immediately above in relation to the interpretation of the Hall data presented in Figure 4. There has been a good deal of work on the one-band t–J model; and in particular Anderson[15] has conjectured that it may have properties resembling the so-called Luttinger liquid, which is a well established picture in strongly correlated one-dimensional liquids. One important feature of the Luttinger liquid is that, unlike the Fermi liquid model, it does not have a 'large' Fermi surface. This fact alone seems to the present reviewer to rule out such models as applicable to the normal state in the superconducting regime of high T_c materials. For angle-resolved photemission experiments can leave no doubt that the Fermi surface is large. Of course, this does not mean that one can use a picture of non-interacting Fermions. One expects, in particular, that the discontinuity in the momentum distribution at the Fermi surface, q say; unity in the non-interacting Fermi gas, will be strongly reduced by interactions in the electron or hole liquids. If E_f is the Fermi energy, one can expect temperature effects then to be greatly enhanced in the electron or hole liquids, since $k_B T$ is to be compared not with E_f as for non-interacting Fermions, but with qE_f as for heavy Fermions[16,17]. Either in the Luttinger liquid, or in the regime of Wigner crystallization[18], the discontinuity q goes to zero, though 'memory' of the Fermi surface remains through singularities in the momentum distribution at the Fermi surface.

While the 'large' Fermi surface seems to exclude the possibility that the normal state of the high T_c materials is a Luttinger liquid, other criticisms of the limitations of the t–J model have been made through the magnetic measurements reported at the end of Section 2 above[19].

In the present writer's judgment, the most promising approach to date, in which there appears to be a realistic account of the solid-state chemistry built in, resides in the work of Stechel and Jennison[8]. Their work leads to the separation of the magnetic properties into that of the electron or hole liquid, plus a (renormalized) Cu sublattice Heisenberg antiferromagnetism, in accord with the analysis of experiments by Johnston[7]. Secondly, their model, for realistic parameters, seems to exclude the spin polaron model explicitly for the high T_c materials. However, the pairing mechanism is subtle*, requiring a careful account of the 'spin hybrid' nature of the wave function describing the electron or hole liquid flowing through the short-range antiferromagnetic array of Cu sublattice spins.

5 SUMMARY AND PROPOSALS FOR FURTHER WORK

Key issues that appear to be clearly resolved by experiment plus theory to date are:

i) The clearcut separation of magnetism into (A) an electron or hole liquid contribution and (B) a Heisenberg type contribution from the Cu spin sublattice in $La_{2-x}Sr_xCuO_{4-y}$ high T_c materials.

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* *Note added in proof.* See, for instance, Dagotto, Kampf and Schrieffer (*Phys. Rev. Lett.*, **67**, 2918 (1991)).

ii) The 'large' Fermi surface in the normal state revealed by angle-resolved photoemission experiments. This appears to rule out the possibility of the Luttinger liquid being involved in the normal state of the high T_c materials. Of course, in a Fermi liquid picture, there is little doubt that the discontinuity, q say, in the momentum distribution at the Fermi surface is greatly reduced from the value unity for a non-interacting Fermi liquid[20].

iii) While the Hall effect is 'anomalous',* the Mott–Hubbard picture seems inappropriate, because again it leads to a 'small' Fermi surface, in disagreement with the experiments in (ii) immediately above.

Matters that are in urgent need of clarification are:

a) Can a small discontinuity q 'explain' the linear dependence of the resistivity shown in Figure 3 down to such low temperatures?

b) Can one understand why the slope of R_H^{-1} in Figure 4 is intimately connected with T_c?

c) Can one measure the discontinuity q by Compton scattering[21,22], or, less favourably because of the distortion of the electron liquid by the probe, by positron annihilation?

d) Is the pairing mechanism for superconductivity spin driven; through some such mechanism as provided by the 'spin hybrids' of Stechel and Jennison[8]?

e) Can Wigner crystallization of electrons or holes occur at low temperatures, and thereby influence the form of T_c versus carrier concentration p as in Figure 2?

f) Is heavy Fermion theory, such as appears to work in discussing the heavy alkalis approaching the metal–insulator transition along the liquid–vapour coexistence curve[17,23], relevant to interpreting the properties of normal state high T_c materials?

While a lot remains to be done, the firm conclusions (i)–(iii) drawn above appear now to narrow down greatly the possibilities open for realistic future studies.

Acknowledgement

The author wishes to thank Professor Yu Lu of ICTP, Trieste, for sending him a copy of his own review[12], which came when this present review was nearing completion, and undoubtedly added to the writer's knowledge of this area.

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