Giant electron-electron scattering in the Fermi-liquid state of Na$_{0.7}$CoO$_2$

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Electron behavior in the layered cobaltate Na$_x$CoO$_2$ shows evidence of strong electron-electron correlations: the specific heat at low temperature points to a significant mass enhancement [1]; the thermopower is ten times larger than that of typical metals at 300 K [2,3]; the material can be made superconducting by intercalation with water [4]. These and other observations have stimulated extensive interest in this material and a quest for possible new electronic phases [5].

A fundamental question is whether these strong electron correlations can be captured by the standard model of metals, namely a Fermi-liquid (FL) description of the ground state and low-energy excitations. A FL description is found to be generally valid for heavy-fermion materials, for example, even though correlations in these systems lead to a huge renormalization of the electron effective mass. On the other hand, such a description is not generally valid for cuprates, except at the highest carrier concentrations. In this Letter, we report on two tests of FL theory applied to Na$_x$CoO$_2$. The first is a test of the Wiedemann-Franz (WF) law, which determines whether the delocalized fermionic excitations of the system carry charge $e$ and are therefore the usual Landau quasiparticles. The second is a measurement of electrical resistivity at low temperature, which looks at the lifetime of these quasiparticles and determines whether the electron-electron scattering rate varies as $T^2$. We find that the WF law is satisfied and we observe a clear $T^2$ regime in the resistivity: $\Delta \rho = \rho - \rho_0 = AT^2$. What is striking is the huge value of the coefficient $A$. When normalized by the quasiparticle effective mass, it is two orders of magnitude larger than in heavy-fermion materials, such that the Kadowaki-Woods ratio reaches an unprecedented value: $A/\gamma^2 \approx 600 \mu\Omega \text{ cm mol}^{-2} \text{ K}^{-2} / \text{ J}^2$.

Na$_x$CoO$_2$ has a hexagonal layered structure consisting of stacked two-dimensional CoO$_2$ planes separated by spacer layers of Na$^+$ ions. The Co ions in each CoO$_2$ plane are arranged on a triangular lattice. In the undoped CoO$_2$ (without Na), each Co atom is in the Co$^{4+}$ valence state with spin 1/2, and the material is speculated to be a Mott insulator. Due to the triangular geometry, those spins are frustrated. With Na doping, each dopant atom contributes one electron, changing Co$^{4+}$ to a spinless Co$^{3+}$ state. The effect of doping is to modify spin correlations and introduce mobile charge carriers, just as in cuprates, but also relax magnetic frustration, so that a rich interplay of spin and charge degrees of freedom is expected.

Single crystals of Na$_x$CoO$_2$ were grown from NaCl flux according to a procedure described elsewhere [6]. The Na concentration was determined to be $x = 0.7$ from a measurement of the $c$-axis lattice parameter (where $c = 10.94 \text{ Å}$), using the calibration in Ref. [6]. Two samples, A and B, were cut to rectangular shapes with $\sim$nm dimensions in the $ab$ plane and 20-50 $\mu$m along the $c$ axis. Contacts were made with silver epoxy, diffused at $500 ^\circ\text{C}$ for 1 hour, and were used to measure both electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$ in a dilution refrigerator down to 40 mK. The contact resistance was typically $\approx 0.1 \Omega$ at low temperature. The thermal conductivity was measured using a standard four-wire steady-state method with two RuO$_2$ chip thermometers calibrated in situ against a reference Ge thermometer. Currents were made to flow in the $ab$ plane and the magnetic field was applied parallel to the current direction.

In Fig. 1, we show the temperature dependence of the in-plane conductivity below 1.2 K, both electrical, plotted as $L_0/\rho(T)$ using the Lorenz number $L_0$ (see below), and thermal, plotted as $\kappa(T)/T$, in a magnetic field $H = 0$ and 10.5 T. There are two contributions to thermal conduction, coming respectively from electrons and phonons. In the limit of electrons being scattered predominantly by defects (e.g. Na impurities), the former will be linear in $T$. In the limit of phonons being scattered predominantly by electrons, the usual case for metals, phonon conduction is quadratic in $T$. This is in-
satisfied in Na$_2$-cuprates do eventually show a purely quadratic dependence $\rho = \rho_0 + AT^2$.

The in-plane resistivity $\rho(T)$ of Na$_{0.7}$CoO$_2$ at low temperature is shown in Fig. 2 for different values of the magnetic field, plotted as $\rho - \rho_{\text{offset}}$ vs. $T^2$. A $T^2$ regime is clearly observed for all fields, below a crossover temperature $T_0$ that grows with field. The field dependence of $T_0$ and $A$ is shown in Fig. 3; $T_0$ goes roughly linearly from $T_0 = 1$ K at $H = 0$ to $T_0 = 4$ K at $H = 16$ T while $A$ decreases from 0.96 to 0.22 $\mu$Ω cm K$^{-2}$. (The low value of $T_0$ explains why the $T^2$ dependence had not been seen in previous studies [11, 12].) The observed relation $\Delta \rho = AT^2$ indicates that the behavior of electrons in this system is well described by FL theory. The remarkable aspect is that the magnitude of the electron-electron scattering is enormous: in zero field, $A = 1.0 \mu$Ω cm K$^{-2}$. This is as large as in heavy-fermion systems, where the strong quasiparticle-quasiparticle scattering is due to the enormous density of states at the Fermi energy, as measured by the residual linear term in the specific heat, $\gamma = C/T$ as $T \to 0$, or equivalently the huge effective mass, $m^*$, as measured for example by the de Haas-van Alphen effect. In these materials, $A$ is found to be roughly proportional to $\gamma^2$. In UPt$_3$, for example, the relation $A \propto \gamma^2$ holds very well as a function of pressure [13]. In fact quite generally, the ratio $r_{KW} \equiv A/\gamma^2$, known as the Kadowaki-Woods ratio, has been shown to
have a nearly universal value of about 10 $\mu$Ω cm mol$^2$ K$^2$ / $J^2 \equiv a_0$ in heavy-fermion systems 14 15 (where $\gamma$ is measured per mole of magnetic ion).

In Fig. 4, a log-log ("Kadowaki-Woods") plot of $A$ vs. $\gamma$ is reproduced for a number of materials. In such a plot, it is important to take into account the effect of anisotropy, since $A$ is in general dependent on the current direction whereas $\gamma$ is an average over all directions on the Fermi surface. In the 3D metal UPt$_3$, for example, that hexagonal crystal structure leads to a mass tensor anisotropy of 2.7 which is reflected in the conductivity of the FL regime (below $T_0 \simeq 1.5$ K), where one finds $A = 0.55 (1.55) \mu$Ω cm K$^{-2}$ for a current parallel (perpendicular) to the hexagonal $c$-axis 16. In Fig. 4, we use the lower value (direction of maximum conductivity) and $\gamma = 0.44$ J / mol K$^2$ 13, so that $r_{KW} = 0.28 a_0$. In quasi-2D systems, transport anisotropy can be much more extreme. The best characterized example of a Fermi liquid state with quasi-2D conductivity is the layered ruthenate Sr$_2$RuO$_4$ 16. Conduction perpendicular to the RuO$_2$ planes is only coherent at low temperature, and the mass tensor anisotropy of the Fermi surface is 1000 or so. This gives rise to a FL regime below $T_0 \simeq 20$ K with $A \simeq 0.006 (0) \mu$Ω cm K$^{-2}$, for in-plane (out-of-plane) transport 16. Given that the quasiparticle states essentially all have wavevectors in the plane, it only makes sense to compute a Kadowaki-Woods ratio for in-plane transport: with $\gamma = 0.04$ J / mol K$^2$ 16, we get $r_{KW} \simeq 0.4 a_0$.

The striking fact about the quasi-2D cobalt oxide Na$_x$CoO$_2$ is that although it has the same $\gamma$ as the quasi-2D ruthenium oxide, its in-plane $A$ coefficient is two orders of magnitude larger, i.e. of the same magnitude as in heavy-fermion systems. Indeed in Na$_{0.7}$CoO$_2$, $\gamma = 0.04$ J / mol K$^2$ (per mole of Co) 11, so that the Kadowaki-Woods ratio is more than 100 times larger than in Sr$_2$RuO$_4$: $r_{KW} \simeq 60 a_0$! This reveals that the strongest electron correlations in Na$_x$CoO$_2$ are responsible for enhancing not so much the effective mass of quasiparticles as their scattering rate. Enhanced values of $r_{KW}$ beyond the typical value of 10 $\mu$Ω cm mol$^2$ K$^2$ / $J^2$ have been seen in a few cases. We now consider these examples to suggest possible mechanisms for the huge $r_{KW}$ value in Na$_{0.7}$CoO$_2$.

The first possible mechanism is proximity to a quantum critical point (QCP). In the heavy-fermion material YbRh$_2$Si$_2$, a magnetic-field-induced QCP occurs when antiferromagnetic order is suppressed by applying a field greater than a critical field $H_c$ 17. This leads to a divergence of both $A$ and $\gamma$ as $H \to H_c$, where $A \sim (H - H_c)^{-a}$, with power $\alpha = 1.0$. The value of $H_c$ can be made very small (30 mT) by substituting 5% of Si for Ge. In YbRh$_2$(Si$_{0.95}$Ge$_{0.05}$)$_2$ 17, $r_{KW}$ is roughly independent of field at large values of the field: it is constant at 0.54 $a_0$ for $(H - H_c)/H_c > 10$.

However, as the field is lowered towards $H_c$, a distinct rise in $r_{KW}$ is observed, reaching a value of 2 $a_0$ at $(H - H_c)/H_c \simeq 1$. A similar field-tuned QCP is observed in the heavy-fermion material CeCoIn$_5$ 18 19, with $H_c = 5.1$ T and $\alpha = 4/3$, where one finds $A = 7.5 (1.0) \mu$Ω cm / K$^2$ 18 and $\gamma = 1.2 (0.64)$ J / mol K$^2$ 19, so that $r_{KW} = 0.52 (0.24) a_0$ at $H = 6 (9)$ T. So here again a field-induced enhancement of $r_{KW}$ is observed as one approaches the QCP. It is interesting to note that a similar effect is observed in Na$_{0.7}$CoO$_2$. In Fig. 3, the coefficient $A$ determined from data in Fig. 2 is plotted as a function of magnetic field.

![FIG. 3: Field dependence of the $T^2$ coefficient $A$ (in $\Delta \rho = AT^2$), and the upper limit of the $T^2$ range, $T_0$ (arrows in Fig. 2), for sample A. Lines are guides to the eye.](image-url)

![FIG. 4: Kadowaki-Woods plot of coefficient $A$ (in $\Delta \rho = AT^2$) vs. $\gamma$, the residual linear term in the specific heat ($\gamma = C/T$ as $T \to 0$), for a number of metals. The three lines are lines of constant Kadowaki-Woods ratio $r_{KW}$ = $A/\gamma^2$, for values of 0.5, 5 and 50 $a_0$, as indicated. The first line at 0.5 $a_0$ is characteristic of heavy-fermion materials and also accounts for the quasi-2D Fermi liquid Sr$_2$RuO$_4$; the second line at 5 $a_0$ corresponds to the highest values observed until now (typically in systems with magnetic frustration or close to a Mott insulator); the third line at 50 $a_0$ shows the order-of-magnitude larger value found in Na$_{0.7}$CoO$_2$. (The data used in this plot are referenced in the text.) The data for YbRh$_2$Si$_2$ is for a sample doped with 5% Ge, for which the QCP is pushed to very low fields (see text).](image-url)
While there is no divergence per se, a five-fold increase is nevertheless observed as $H$ goes from 16 to 0 T. Using the specific heat data of Brühwiler et al. [14], where $\gamma = 0.04 (0.025) J / \text{mol K}^2$ in $H = 0 (14)$ T, we get $r_{KW} = 60 (40) a_0$, at $H = 0 (14)$ T. This therefore suggests that one interpretation of the strong field dependence of $A$ is a close-by QCP of magnetic nature. In support of this interpretation, there is evidence of a spin density wave transition in Na$_2$CoO$_2$ at a slightly higher Na concentration, namely $x = 3/4$ [20, 21, 22], and $\rho(T)$ below 20 K is indeed steepest at $x = 0.75$ [23], while $\gamma$ remains constant between $x = 0.55$ [1] and 0.7 [11]. Quantum critical behaviour has also been theoretically predicted in Na$_2$CoO$_2$ based on discrepancies between ferromagnetism predicted by density-functional calculations and the measured paramagnetic ground state [24].

A second comparison, to the transition metal oxide LiV$_2$O$_4$, is highly suggestive. Both the cubic spinel structure of LiV$_2$O$_4$, in which V ions lie on a sub-lattice of corner-sharing tetrahedra, and the layered structure of Na$_2$CoO$_2$, in which Co ions lie on a two-dimensional triangular lattice, give rise to strong magnetic frustration. The extraordinarily heavy mass observed in the FL state of LiV$_2$O$_4$ - characterized by $\gamma \approx 0.175 J / \text{mol K}^2$ (per mole of V), $A = 2.0 \mu \Omega \text{cm} / \text{K}^2$ and $T_0 \approx 1.5 K$ [24] - has been attributed to geometric frustration [24, 25]. Although this has not been emphasized, this material has also held the record for the largest Kadowaki-Woods ratio until now: $r_{KW} = 6.5 a_0$. This is one order of magnitude larger than in typical heavy-fermion materials - like YbRh$_2$Si$_2$ (0.54), UPt$_3$ (0.28) and CeCoIn$_5$ (0.24) - but still one order of magnitude smaller than in Na$_2$CoO$_2$. The latter discrepancy might have to do with the different dimensionalities of the electron system in these two oxides: 3D in LiV$_2$O$_4$, 2D in Na$_2$CoO$_2$.

Finally, we mention a third instance of anomalously large Kadowaki-Woods ratios: proximity to a Mott insulator. The transition metal oxide V$_2$O$_3$ is close to a metal-insulator transition and it has $\gamma \approx 0.032 J / \text{mol K}^2$ (per mole of V) and $A = 0.05 \mu \Omega \text{cm} / \text{K}^2$, so that $r_{KW} \approx 5 a_0$ [15]. Replacing Sr by Ca in Sr$_2$RuO$_4$ produces a Mott insulator. By gradually replacing Sr, Nakatsuji et al. have shown how $r_{KW}$ in Ca$_{2-x}$Sr$_x$RuO$_4$ goes from 0.4 $a_0$ at $x = 2$, to $a_0$ at $x = 0.5$, to a value as large as 7 $a_0$ at $x = 0.2$ [26]. For $x < 0.5$, a structural transition appears to induce a Mott gap on part of the Fermi surface, with concomitant $S = 1/2$ localized moments, as evidenced by a decrease of $\gamma$ with decreasing $x$. The authors interpret the large enhancement of $A$ near the Mott insulator as a combination of the narrowing of the remaining conduction band and the additional scattering of conduction electrons on these (antiferromagnetically-coupled) localized moments [26]. In this respect, we note that cuprates, the most infamous doped Mott insulators, also exhibit anomalously large $r_{KW}$. Specifically, in overdoped La$_{2-x}$Sr$_x$CuO$_4$ with $x = 0.3$, the FL state is characterized by $\gamma \approx 7 \text{mJ} / \text{mol K}^2$, $A \approx 2.5 \text{n} \Omega \text{cm} / \text{K}^2$ and $T_0 \approx 1.5 K$ [10], so that $r_{KW} \approx 5 a_0$. Although this doping value ($x = 0.3$) is not usually thought to be close to the Mott insulator ($x = 0$), $r_{KW}$ is still 10 times larger than in the isostructural material Sr$_2$RuO$_4$. (Note that in none of these cases is geometric frustration an issue.)

In conclusion, Na$_2$CoO$_2$ with $x = 0.7$ adopts a Fermi-liquid state at low temperature that is characterized by the largest Kadowaki-Woods ratio ever observed. Comparison with other materials suggests that the unprecedented magnitude of the electron-electron scattering is due either to magnetic frustration or to the proximity of a nearby magnetic quantum critical point or a Mott insulator. Theoretical exploration of the impact of magnetic frustration on electron scattering, including the role of magnetic field and reduced dimensionality, would be most useful.

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