Metamagnetism of itinerant electrons in multi-layer ruthenates

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Abstract. – The problem of quantum criticality in the context of itinerant ferro- or metamagnetism has received considerable attention (Grigera S. A. et al., Science, 294 (2001) 329; Pfleiderer C. et al., Nature, 414 (2001) 427). It has been proposed that a new kind of quantum criticality is realised in materials such as MnSi or Sr\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7}. We show, based on a mean-field theory, that the low-temperature behaviour of the \(n\)-layer ruthenates Sr\textsubscript{\(n+1\)}Ru\textsubscript{n}O\textsubscript{\(3n+1\)} can be understood as a result of a Van Hove singularity (VHS). We consider a single band whose Fermi energy, \(E_F\), is close to the VHS and deduce a complex phase diagram for the magnetism as a function of temperature, magnetic field and \(E_F\). The location of \(E_F\) with respect to the VHS depends on the number of layers or can be tuned by pressure. We find that the ferromagnetic quantum phase transition in this case is not of second but of first order, with a metamagnetic quantum critical end-point at high magnetic field. Despite its simplicity, this model describes well the properties of the uniform magnetism in the single-, double- and triple-layer ruthenates. We would like to emphasise that the origin of this behaviour lies in the band structure.

Introduction. – The issue of metamagnetism in itinerant electron systems was studied both theoretically [1, 2] and experimentally [3] long ago. Recently, the investigation of metamagnetism in two compounds, MnSi [4] and Sr\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7} [5, 6], has revived interest in this phenomenon, considering it from a new point of view. It has been suggested that these systems might display a new type of quantum criticality, connected with a so-called quantum critical end-point (QCEP), in the vicinity of which the Landau Fermi-liquid theory of metals breaks down. In fact the field \(H_m(T)\) initiating the metamagnetic transition, the abrupt increase of the magnetisation, defines a line of first-order transitions in the field-temperature \((T)\) plane without any symmetry breaking. The first-order line ends in a critical end-point \((H_c, T_c)\). A QCEP occurs if \(T_c\) is suppressed to zero as a function of an additional parameter, such as the pressure or the chemical composition of the material.

While theoretical results concerning the properties of the QCEP have been obtained recently on the basis of phenomenological, low-energy field theories [7], to our knowledge no
discussion of the microscopic origin of such a QCEP has been provided yet. In the following, we present a model which gives rise to a QCEP of the above kind, which we will discuss within a simple Hartree-Fock theory. This model is based on a system with a single, two-dimensional electron band where the Fermi level is close to a Van Hove singularity (VHS). Our results for the magnetisation as a function of field, temperature and the band filling are in qualitative agreement with observed properties of the two- and three-layer ruthenate compounds \[8,9\], and suggest that the general magnetic phase diagram of \( n \)-layer ruthenates might be understood in terms of band structure properties.

**Mean-field theory of itinerant uniform magnetism.** We consider a single-band model of electrons interacting via an on-site Coulomb repulsion \( U \). In the Hartree-Fock (or mean-field) approximation, the free energy per unit cell \( f \) is given as a function of the particle density \( n \), the uniform magnetisation \( m \) (in units of \( g\mu_B \) per unit cell) and the temperature by

\[
f_{HF}(n, m, T) = f_0(n, m, T) + U n \n \]

where \( n \n = n/2 \pm m \) are the densities of up- and down-spin electrons, respectively, and \( f_0 \) is the free energy in the absence of interactions, i.e.

\[
f_0(n, m, T) = \sum_{\sigma = \uparrow, \downarrow} \left[ \Omega_0(\mu_\sigma, T) + \mu_\sigma n_\sigma \right],
\]

where \( \Omega_0(\mu_\sigma, T) \) is the grand-canonical potential and \( \mu_\sigma(n_\sigma, T) \) are the chemical potentials for the two species of electrons in the absence of interactions. The only information about the band structure which enters the mean-field theory is the density of states (DOS) as a function of energy, \( \rho(\epsilon) = 1/V \sum_k \delta(\omega - \epsilon_k) \), where \( \epsilon_k \) is the electron dispersion and the sum is over the first Brillouin zone. Given \( \rho(\epsilon) \), one obtains \( \Omega_0(\mu_\sigma, T) = -k_B T \int \rho(\epsilon) \ln (1 + e^{-\beta(\epsilon - \mu_\sigma)}) \), where \( k_B \) is the Boltzmann constant and \( \beta = (k_B T)^{-1} \). The chemical potentials \( \mu_\sigma(n_\sigma, T) \) are given implicitly by

\[
n_\sigma = -\partial_{\mu_\sigma} \Omega_0 = \int d\epsilon \rho(\epsilon) f_T(\epsilon - \mu_\sigma),
\]

where \( f_T(\epsilon) = 1/(\exp[\beta \epsilon] + 1) \) is the Fermi function.

In the following, we omit the suffix “HF” in \( f_{HF} \). Once the free energy is determined, we obtain the thermodynamic equation of state

\[
h = \partial_m f = \mu_\uparrow - \mu_\downarrow - 2U m,
\]

where \( h \) is the external magnetic field multiplied by \( g\mu_B \). Equation (4) may be solved for \( m \) to obtain the magnetisation as a function of \( n, T \) and \( h \). The thermodynamically stable solution minimises the Gibbs free energy, \( g = f - hm \).

A first-order transition is characterised by a discontinuous jump of the magnetisation, whereas a smooth metamagnetic transition occurs if the differential susceptibility \( \chi = \partial m/\partial h \) has a (more or less pronounced) maximum. The susceptibility is obtained from

\[
\frac{1}{\chi} = \partial_m^2 f = \sum_\sigma \frac{1}{A_0(\mu_\sigma, T)} - 2U,
\]

where \( A_0(\mu, T) = \int d\epsilon \rho^{(n+1)}(\epsilon) f_T(\epsilon - \mu) \). Note that \( \lim_{T \to 0} A_n(\mu, T) = \rho^{(n)}(\mu) \), where \( \rho^{(n)}(\mu) \) denotes the \( n \)-th derivative of the DOS at the Fermi level. Because \( \partial_m \chi|_{m=0} = 0 \) and \( \lim_{m \to -\infty} \chi = 0 \), a sufficient (but not necessary) condition for either smooth or first-order metamagnetism is given by \( \partial_m^2 \chi|_{m=0} > 0 \), which is equivalent to \( \partial_m^4 f|_{m=0} < 0 \) or
$A_0A_2 > 3(A_1)^2$, where $A_n$ is evaluated at $\mu = \mu_1 = \mu_{1\uparrow}$, i.e. in the absence of magnetisation. At zero temperature, this is equivalent to the condition

$$\rho\rho'' > 3(\rho')^2,$$

(6)

which has been discussed by Wohlfarth and Rhodes [1]. The condition is clearly satisfied if the DOS is large and has a strong positive curvature at the Fermi level.

Such a positive curvature also gives rise to two unusual finite-temperature properties. First, $\chi(T)\left|_{m=0}\right.$ is not monotous, but has a maximum as a function of $T$. Second, the entropy $s = -\partial_T f$ at low temperatures does not decrease monotonously with the magnetisation, but has a maximum at a finite $m$. Both phenomena are related to the fact that, if $\rho(\varepsilon)$ is positively curved, the average DOS in a finite region around $\varepsilon_F$ is higher than the DOS at the Fermi level. A sufficient condition for the two properties mentioned above is given by $\partial_T^2 \rho_m f\left|_{m=T=0}\right. < 0$ or $\rho\rho'' > (\rho')^2$, which is a weaker condition than eq. (6).

Equation (6) is satisfied if, for example, the Fermi level occurs at a local minimum of the DOS. This case probably applies to MnSi [10]. Another example, which we wish to address here, occurs if the Fermi level is close to a VHS. This is the case for the Sr-ruthenates which as layered perovskite systems represent quasi–two-dimensional electron systems. In two dimensions the VHS is logarithmic, i.e. the DOS has the asymptotic behaviour $\rho(\varepsilon) = \frac{1}{\varepsilon T} \ln |\frac{W_2}{\varepsilon}|$, where $W_{1,2}$ are two parameters with units of energy, which are both of the order of the bandwidth\(^{(1)}\). For simplicity, we choose $W_1 = W_2 = W$ in the following, and we extend the logarithmic form of the DOS from $\varepsilon = -W$ to $+W$.

One way to study phase transitions is to develop $f$ in powers of $m$. This has been performed previously for related systems [1,2,10], but the application of such a procedure can be complicated. At least at zero $T$, this approach is not successful in the present case, because as soon as eq. (6) is satisfied, $\partial_m^n f\left|_{m=T=0}\right. \leq 0$ for all $n \geq 4$. In fact, $f(m)|_{T=0}$ is not analytic at the specific value of $m$ where one of the Fermi levels crosses the VHS.

Results. – Despite its simplicity, our model yields a complex mean-field phase diagram. In fig. 1, we show the phase diagram as a function of temperature, magnetic field and the parameter $x$, which is the difference between the actual electron density and the density at Van Hove filling, i.e. $x = n - 2$.

If the system is very close to the VHS, we find the usual Stoner instability, i.e. a second-order transition as a function of temperature. The line of second-order transitions within the $(T, x)$-plane of the phase diagram is characterised by a diverging susceptibility, or equivalently $U A_0(\mu(x, T), T) = 1$. If the system is pushed further away from the VHS, the simple picture of a ferromagnetic low-temperature and a paramagnetic high-temperature phase is no longer valid, and we find a weak re-entrant behaviour, i.e. the system is ferromagnetic for intermediate temperatures, $T_1 < T < T_2$. The reason for this behaviour lies in the entropy anomaly discussed above. The re-entrant behaviour occurs only in a very narrow range of $x$ ($0.089 < x < 0.091$ for $U = 0.2W$).

At low temperatures, the (re-entrant) transition between the ferro- and the paramagnetic phase is of first order, i.e. it occurs due to the crossing of two minima of $g(m) = f(m) - hm$. For example, the quantum phase transition as a function of $x$ at $T = h = 0$ occurs at $x \approx 0.089$, whereas the Stoner criterion $U\rho(\varepsilon_F) = 1$ would give a slightly smaller value, $x \approx 0.081$. A metastable ferromagnetic state, which is present in the paramagnetic region close to the first-order transition, gives rise to a first-order transition in an external magnetic field. This transi-

\(^{(1)}\)As an example, the $\gamma$-band of Sr$_2$RuO$_4$ is well approximated by a two-dimensional tight-binding model with nearest-neighbour hopping $t = 0.17$ eV and diagonal next-nearest-neighbour hopping $t' = 0.08$ eV. For this model we find $W_1 = 2\pi^2 \sqrt{t^2 - 4|t'|^2} \approx 1.14$ eV and $W_2 \approx 0.92$ eV.
Fig. 1 – The phase diagram for $U = 0.2W$ as a function of temperature, magnetic field and $x$, the separation of the electron density from the Van Hove filling. The transition from ferro- to paramagnetic behaviour changes from second to first order. The grey surface indicates a first-order metamagnetic transition (i.e. a jump in the magnetisation) and terminates at a line of critical end-points. This line is suppressed rapidly to low temperatures and finally reaches zero temperature at a QCEP. The inset shows a detailed section of the phase diagram projected on the $(x, T)$-plane.

Fig. 2 – Magnetisation as a function of external field for three different fillings and for temperatures $k_B T = 0, 1, 2, 3, 4, 5 \cdot 10^{-3}W$.

Fig. 1

Fig. 2

The critical field of the transition decreases slightly with temperature at fixed values of $x$. The line of first-order transitions (at fixed $x$) terminates at a critical end-point $(h_c(x), T_c(x))$, which forms a line of critical end-points in the parameter space including $x$. This line of critical end-points is determined by the equations: $\partial^2 m f = \partial^3 m f = 0$ and eq. (4), which must be solved for $h$, $T$ and $m$ at a given value of $x$. The second derivative is given in eq. (5) and an explicit expression for the third derivative is $\partial^3 m f = A_{1}(\mu_{\uparrow})/A_{0}(\mu_{\uparrow}) - A_{1}(\mu_{\downarrow})/A_{0}(\mu_{\downarrow})$.

With increasing separation from the Van Hove filling, the critical point moves rapidly to lower temperatures and higher fields. Finally, the line of critical end-points reaches zero temperature, thus giving rise to a QCEP at the point $(x_{qc}, h_{qc})$. The low-temperature limit is more involved. In fact, the equation $\partial^3_m f = 0$ must be replaced at zero temperature by the requirement that one of the two spin bands, for example the spin-down band, is at Van Hove filling, i.e. $\mu_{\downarrow} |_{QCEP} = 0$, which implies that $x_{qc} = 2m_{qc}$. As a consequence, $\partial^3_m f$ is not zero at the QCEP and actually has a pole. We find

$$x_{qc} = \left(1 + \frac{W}{2U}\right) e^{-\frac{W}{2U}},$$  

$$2h_{qc} = (W - 2U)e^{-\frac{W}{2U}},$$  

(7)  

(8)
Fig. 3 – Zero-field spin susceptibility as a function of temperature for three different fillings, $x = 0.095$, 0.1 and 0.11 (from top to bottom).

where $W$ is the energy parameter in the model DOS. For $U = 0.2W$, this yields $x_{qc} \approx 0.29$ and $h_{qc} \approx 25 \cdot 10^{-3}W$. The basic structure of the phase diagram of fig. 1 is invariant inside the range $0 < U < W/2$, although the details depend strongly on $U$. For $U > W/2$, both first-order metamagnetism and quantum criticality disappear.

Within our model and choice of parameters, the QCEP lies outside the experimentally accessible region. Accessing this point would require a magnetic field in the order of 200 tesla, and even if such enormous fields could be created, the metamagnetic behaviour (i.e. the anomaly in $m(h)$) is negligible. We find that $T_c$ is suppressed exponentially as the QCEP is approached, i.e. $T_c(x) \sim \exp[\alpha/(x - x_{qc})]$ with $\alpha = (W/2\pi)^3 \exp[-W/2\pi] \approx 1.28$. This leads to critical end-points at extremely low temperatures for realistic values of the magnetic field, which are practically indistinguishable from the true QCEP. The Fermi level, $\mu$, at the critical end-point vanishes even faster than $T_c$ for $x \rightarrow x_{qc}$.

In fig. 2, we show the equilibrium magnetisation as a function of the magnetic field for three different fillings and for various temperatures. At $x = 0.09$, the system is in the re-entrant ferromagnetic regime. At very low temperatures, a first-order magnetic transition can be found at a small but finite field. A metastable magnetic phase also exists in the absence of the external field. True equilibrium ferromagnetism is established only at intermediate temperatures, and there is a second-order phase transition towards a high-temperature paramagnetic state.

For $x = 0.1$, the system is in the metamagnetic regime. At low temperatures there is a first-order metamagnetic transition. Both the critical field of this transition and the size of the magnetisation jump are decreasing functions of temperature. The discontinuity is transformed into a smooth metamagnetic crossover above the critical temperature, $k_BT_c \approx 1.2 \cdot 10^{-3}W$, and at still higher temperatures, the normal paramagnetic behaviour is recovered. Further away from the Van Hove filling, at $x = 0.11$ (fig. 2c)), the behaviour is similar, but the metamagnetic transition occurs at higher fields and $T_c$ is reduced.

From figs. 2b) and c), we observe that the linear response to low fields is not a monotonous function of temperature, but has a maximum at a finite temperature $T^*$ which is higher than $T_c$. For fillings close to the re-entrant ferromagnetic regime, $k_BT^*$ approaches $3.2 \cdot 10^{-3}W$, the temperature where ferromagnetism first appears, as $x$ is lowered. At this point, which corresponds to a second-order ferromagnetic transition, the susceptibility is in fact a diverging quantity. For larger values of $x$, the peak in $\chi(T)$ is much less pronounced and $T^*$ increases (fig. 3). A very broad maximum remains even for fillings much larger than $x_{qc}$.

Comparison with experiment. – In view of the metamagnetic behaviour of the multi-layer strontium-ruthenates (the layered perovskite compounds $\text{Sr}_{1+n}\text{Ru}_n\text{O}_{3n+1}$), it is natural to
concentrate on the electronic band which is related to the $\gamma$-band of the single-layer compound. This band, which originates from the $4d_{xy}$ orbitals of Ru, lies close to a VHS. The double-layer compound $\text{Sr}_3\text{Ru}_2\text{O}_7$ has a modified band structure which preserves two bands with the basic $\gamma$-band structure. Band structure calculations suggest that one band is moved closer to the VHS [11, 12]. It is natural to assume that this trend of approaching the VHS in one band progresses with increasing number $n$ of layers in each unit cell, so that $n$ is a tuning parameter for the variable $x$ in one of the bands. Other aspects, such as a possible change in the ratio between the bandwidth and the Coulomb repulsion or more complex multi-band physics, are neglected. In fact a phase diagram very similar to fig. 1, where the filling parameter $x$ is replaced by the pressure, was proposed on purely phenomenological grounds in relation to $\text{Sr}_3\text{Ru}_2\text{O}_7$ [6]. For a given compound, $x$ may also be tuned by external pressure or by chemical pressure, such as the gradual replacement of Sr by the smaller isoelectronic ion Ca.

The magnetisation curves in fig. 2b) are in good qualitative agreement with the observed behaviour in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ [9] for magnetic fields parallel to the $ab$-plane(2). Furthermore, fig. 2c) is consistent with the experimental findings in $\text{Sr}_3\text{Ru}_2\text{O}_7$ [8], where smooth metamagnetism has been observed at fields which are 2-3 times larger than the critical field in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ [9]. We would like to emphasise that the basic, qualitative properties of the double- and triple-layer compounds are in good agreement with our model calculation. Our choice of parameters even yields values of temperature and magnetic field which are of the same order of magnitude as those found in experiment. From our calculations, we expect that a first-order metamagnetic transition should be found at sufficiently low temperatures in $\text{Sr}_3\text{Ru}_2\text{O}_7$, but given the rapid decrease of $T_c$ as a function of $x$, the required temperature is likely to be much smaller than that attained in the experiment.

We stress that in our model the QCEP occurs when one band is at the Van Hove filling. This circumstance may influence unconventional transport properties in the vicinity of the QCEP [5], for non-Fermi-liquid behaviour has been suggested as one consequence of an itinerant electron band being at the Van Hove filling [13–15].

Instead of increasing the number of layers, an alternative approach to the VHS may be through electron doping of the single-layer compound. This was attempted recently by partial replacement of Sr by La [16]. The experimental result indeed shows an enhanced magnetic response as a function of doping, but neither ferromagnetism nor the typical temperature dependence of the susceptibility, with a maximum at finite temperature, was observed. The question of the extent to which the doping may lead to an increase in the itinerant electron density remains to be answered. If the additional electrons remain essentially localised around the dopants, this may yield a similarly enhanced, almost Curie-like, susceptibility [16].

**Conclusion.** – In conclusion, we have presented a mean-field theory of uniform magnetism for a single band of itinerant electrons which is close to a VHS. The resulting phase diagram, as shown in fig. 1, features first- and second-order ferromagnetic transitions, as well as a line of (metamagnetic) critical end-points, which is pushed to zero temperature at a QCEP. Such a phase diagram has been proposed on purely phenomenological grounds in the context of MnSi [4] and multi-layer ruthenates [6], but no microscopic description has been provided yet. Despite its simplicity, our model calculation gives a good qualitative description of the magnetic properties of two- and three-layer ruthenates [8, 9]. The general magnetic behaviour of these materials may thus be explained in terms of band structure properties. A similar scenario applies to MnSi, where the Fermi energy is likely to be associated with a dip in the

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(2) $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ is actually ferromagnetic below 105 K, with an easy axis in the $c$-direction. Metamagnetic behaviour was observed by applying a field parallel to the $ab$-plane. The very different magnetic behaviour parallel and perpendicular to the $c$-axis is an effect of spin-orbit coupling, which is not included in our model.
electron DOS, and to FeSi$_{1-x}$Ge$_x$, which exhibits a transition from a small-gap semiconductor to a metallic ferromagnet with increasing $x$ [17].

Our analysis reveals the remarkable aspect that the QCEP is characterised by the situation in which the chemical potential of one of the bands (minority- or majority-spin) is exactly at the Van Hove filling. This should have non-trivial consequences for the metallic properties close to the QCEP. In particular, transport properties may show non-Fermi-liquid behaviour [13,15], similar to the experimental observation [5].

Finally, we comment that, although the model we have presented captures many of the qualitative features observed in multi-layer ruthenates, it remains a relatively crude simplification. Here we have neglected several aspects, including multi-band effects, spin-orbit coupling and disorder effects, which undoubtedly have a certain role in real materials. One of the most important questions concerns the effects of spin fluctuations, which are neglected within the Hartree-Fock approximation. These aspects are the subject of current studies.

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