Why Ni$_3$Al is an itinerant ferromagnet but Ni$_3$Ga is not

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Ni$_3$Al and Ni$_3$Ga are closely related materials on opposite sides of a ferromagnetic quantum critical point. The Stoner factor of Ni is virtually the same in both compounds and the density of states is larger in Ni$_3$Ga. So, according to the Stoner theory, it should be more magnetic, and, in LDA calculations, it is. However, experimentally, it is a paramagnet, while Ni$_3$Al is an itinerant ferromagnet. We show that the critical spin fluctuations are stronger than in Ni$_3$Ga, due to a weaker $q$-dependence of the susceptibility, and this effect is strong enough to reverse the trend. The approach combines LDA calculations with the Landau theory and the fluctuation-dissipation theorem using the same momentum cut-off for both compounds. The calculations provide evidence for strong, beyond LDA, spin fluctuations associated with the critical point in both materials, but stronger in Ni$_3$Ga than in Ni$_3$Al.

Recent low temperature experiments on clean materials near ferromagnetic quantum critical points (QCP) have revealed a remarkable range of unusual properties, including non-Fermi liquid scalings over a large phase space, unusual transport, and novel quantum ground states, particularly coexisting ferromagnetism and superconductivity in some materials. Although criticality usually implies a certain universality, present experiments show considerable material dependent aspects that are not well understood. \cite{[1]} e.g. the differences between UGe$_2$ and URhGe \cite{[2],[3]} and ZrZn$_2$, \cite{[4]} which both show coexisting ferromagnetism and superconductivity but very different phase diagrams, in contrast to MnSi, where very clean samples show no hint of superconductivity around the QCP. \cite{[5]} Generally, approaches based on density functional theory (DFT) are successful in accounting for material dependence in cases where sufficiently accurate approximations exist. To proceed in this direction it is useful to study benchmark systems for which detailed experimental data are available and which pose challenges to theory. Here we report a study of the closely related compounds Ni$_3$Al and Ni$_3$Ga. Both of these have the ideal cubic Cu$_3$Au $cP4$ structure, with very similar lattice constants, $a = 3.568$ Å and $a = 3.576$ Å, respectively, and have been extensively studied by various experimental techniques. Ni$_3$Al is a weak itinerant ferromagnet, $T_c = 41.5$ K and magnetization, $M = 0.23 \mu_B$/cell ($0.077 \mu_B$/Ni atom) \cite{[6]} with a QCP under pressure at $P_c = 8.1$ GPa, \cite{[7]} while Ni$_3$Ga is a strongly renormalized paramagnet \cite{[8]}. Further, it was recently reported that Ni$_3$Al shows non-Fermi liquid transport over a large range of $P$ and $T$ range down to very low $T$. \cite{[9]}

DFT is an exact ground state theory, and as such should properly describe the magnetic ground states of metals. However, common approximations to DFT, such as the LDA and GGA, are based on the properties of the uniform electron gas at densities that occur in solids. At these densities it is rather stiff with respect to spin fluctuations and is not close to any magnetic instability. As a result, the LDA description of magnetism is at a quasi-classical mean field level, (i.e. Stoner level), and neglects fluctuations due to soft magnetic degrees of freedom. This leads to misplacement of QCPs and overestimates of the magnetic tendencies of materials near QCPs, as well as such known problems as the incorrect description of singlet states in molecules with magnetic ions. In fact, practically all cases where the LDA substantially overestimates the tendency towards magnetism are materials near a QCP \cite{[10],[11],[12],[13]} – a fact that can potentially be used as a screen for materials with large fluctuation effects. \cite{[14]} Previous LDA calculations showed that the magnetic tendency of both materials is overestimated within the LDA, and that Ni$_3$Ga is incorrectly predicted to be a ferromagnet. \cite{[15],[16],[17],[18],[19],[20]} Moreover, as our present results show, in the LDA the tendency to magnetism is stronger in Ni$_3$Ga than Ni$_3$Al, opposite to the experimental trend. This poses an additional challenge to any theory striving to describe the material dependent aspects of quantum criticality. The two materials are expected to be very similar electronically (our results confirm this, and identify the small difference between the two as due to relativistic effects associated with Ga in Ni$_3$Ga). Thus they offer a very useful and sensitive benchmark for theoretical approaches. We use this to test an approach based on the fluctuation dissipation theorem applied to the LDA band structures with an ansatz for the cut-off $q_c$. We find that this approach corrects the ordering of the magnetic tendencies of the materials, and gives the right ground states at ambient pressure as well as a reasonable value of $P_c$ for Ni$_3$Al.

Our LDA calculations were done using the general potential linearized augmented-plane-wave (LAPW) method with local orbital extensions \cite{[21],[22]} in two implementations \cite{[22],[23],[24]}, with the exchange-correlation func-
tional of Hedin-Lundqvist with the von Barth-Hedin spin scaling [25,26]. Up to 816 inequivalent \( \mathbf{k} \)-points were used in the self-consistent calculations, with an LAPW basis set defined by the cut-off \( R_{\text{cut}} K_{\text{max}} = 9 \), plus local orbitals to relax linearization errors. Larger numbers of \( \mathbf{k} \)-points between 2300 and 4060 were used in the Fermi surface integrations. The LDA electronic structure is given in Fig. 1 and Table 1, while results of fixed spin moment calculations of the magnetic properties at the experimental lattice parameters and under hydrostatic compression are given in Figs. 2 and 3. The two compounds are very similar in both electronic and magnetic properties, the main apparent difference being the higher equilibrium moment of Ni\(_3\)Ga (0.79 \( \mu_B \)/f.u. vs. 0.71 \( \mu_B \)/f.u.), in agreement with other full potential calculations. [19,20]

The propensity towards magnetism may be described in terms of the Stoner criterion, \( IN(E_F) \), where \( I \) is the so-called Stoner parameter, which derives from Hund’s rule coupling on the atoms. For finite magnetizations, the so-called extended Stoner model [27], states that to the second order in the spin density the magnetic stabilization energy is expressed as \( \Delta E = M^2 \int_0^M m \, dm/2 \bar{N}(m) - I/4 \), where \( \bar{N}(M) \) is the density of states averaged over the exchange splitting corresponding to the magnetization \( M \). Fitting our fixed spin moment results to this expression, we find \( I_{\text{Al}} \) = 0.385 eV and \( I_{\text{Ga}} \) = 0.363 eV. These gives \( IN(E_F) \) =1.21 and \( IN(E_F) \) = 1.25 for Ni\(_3\)Al and Ni\(_3\)Ga, respectively. Both numbers are larger than 1, corresponding to a ferromagnetic instability, and the value for Ni\(_3\)Ga is larger than that for Ni\(_3\)Al. Importantly, the difference comes from the density of states, since \( I_{\text{Al}} > I_{\text{Ga}} \). In both compounds, magnetism is suppressed by compression, with an LDA critical point at a value \( \delta a/a \sim -0.05 - 0.06 \). In Ni\(_3\)Al, the critical point at \( \delta a/a = -0.058 \) corresponds to the pressure of \( P_c = 50 \text{ GPa, } [28] \) which is much higher than the experimental value. It is interesting that, as in ZrZn\(_2\) [11], the exchange splitting is very strongly \( \mathbf{k} \)-dependent: for instance, in Ni\(_3\)Al at some points it is as small as 40 meV/\( \mu_B \) near the Fermi level, while at the others (of pure Ni d character) it is close to 220 meV/\( \mu_B \).

Notwithstanding the general similarity of the two compounds, there is one important difference near the Fermi level, specifically, the light band crossing the Fermi level in the middle of the \( \Gamma-M \) or \( \Gamma-X \) directions is steeper in Ni\(_3\)Al (Fig. 1). This, in turn, leads to smaller density of states. This comes from a different position of the top of this band at the \( \Gamma \) point, 0.56 eV in Ni\(_3\)Ga and 0.85 eV in Ni\(_3\)Al. The corresponding electronic state is a mixture of Ni \( p \) and Al (Ga) \( p \) states, and is the only state near the Fermi level with substantial Al (Ga) content. Due to relativistic effects, the Ga \( p \) level is lower than the Al \( p \) level and this leads to the difference in the position of the corresponding hybridized state. Note that this is a purely scalar relativistic effect. We checked that including spin orbit does not produce any further discernible difference.

Returning to magnetism, the fixed spin moment calculations provide the energy \( E \) as a function of the magnetization \( M \) (Fig. 2). One can write a Landau expansion for \( E(M) \) as

![FIG. 1. Calculated LDA band structure (top) and density of states (bottom) per f.u. for non-spin-polarized Ni\(_3\)Al (solid lines) and Ni\(_3\)Ga (dotted lines). \( E_F \) is at 0 eV.](image)

![FIG. 2. Energy vs. fixed spin moment for Ni\(_3\)Al and Ni\(_3\)Ga at the experimental lattice parameters. The energy zero is set to the non-spin-polarized value.](image)
\[
E(M) = a_2 M^2/2 + a_4 M^4/4 + a_6 M^6/6 + \cdots
\] (1)

Treating this as a mean-field expression and adding the effects of spin fluctuations [29] leads to renormalization of the expansion coefficients. The renormalized coefficients \(a_i\) are written as power series in the averaged square of the magnetic moment fluctuations beyond the LDA, \(\xi^2\),

\[
\dot{a}_2 = \sum_{i=0}^{n+1} C^{n+1}_{n+1-i} \xi^2 \prod_{k=n}^{n+i} (1 + 2k/3). \tag{2}
\]

\(\xi\) may be estimated by requiring that the corrected Landau functional (2) reproduces the experimental magnetic moment (for \(\text{Ni}_3\text{Al}\)) or experimental magnetic susceptibility (for \(\text{Ni}_3\text{Ga}\)). The “experimental” \(\xi\)’s obtained in this manner are 0.47 and 0.55, respectively, which implies that spin fluctuation effects must be stronger in \(\text{Ni}_3\text{Ga}\) than in \(\text{Ni}_3\text{Al}\).

We shall now make a link between this fact and the electronic structures. A standard formula for estimating \(\xi^2\) comes from the fluctuation-dissipation theorem [30], which establishes that

\[
\xi^2 = (2\hbar/\Omega) \int d^3q \int (d\omega/2\pi) \text{Im} \chi(q, \omega),
\] (3)

where \(\Omega\) is the Brillouin zone volume, and \(\chi\) is the magnetic susceptibility. Using the lowest order expansion for \(\chi\),

\[
\chi_0(q, \omega) = N(E_F) - a q^2 + i \omega / \hbar
\] (4)

\[
\chi^{-1}(q, \omega) = \chi_0^{-1}(q, \omega) - I,
\] (5)

where \(\chi_0(q, \omega)\) is the non-interacting susceptibility, one can derive a formula for \(\xi^2\) [29,30], whose coefficients can be related to the characteristics of the electronic structure [30,31]. The final results reads

\[
\xi^2 = \frac{b v_F^2 N(E_F)^2}{2a^2 \Omega} [Q^4 \ln(1 + Q^{-4}) + \ln(1 + Q^4)],
\] (6)

where \(a = (d^2(N(E_F)q_F^2)/dE_F^2)/12\), \(b = (N(E_F)v^{-1})/2\), \(v_F = \sqrt{3(d^2(N(E_F)v_F^2)}\), \(Q = q_c a/b v_F\), and \(q_c\) is the cutoff parameter for integration in Eq.3. The physical meaning of these parameters is as follows. \(a\) defines the rate at which the static susceptibility \(\chi(q, 0)\) falls away from the zone center, i.e., the extent to which the tendency to ferromagnetism is stronger than that to antiferromagnetism. This translates into the phase space in the Brillouin zone where the spin fluctuations are important. \(b\) controls the dynamic effects in spin susceptibility. The cutoff parameter \(q_c\) is the least well defined quantity in this formalism. One obvious choice is \(q_c = \sqrt{N(E_F)/a}\), because for larger \(q\) the approximation (4) gives unphysical negative values for the static susceptibility. On the other hand, this choice leads to noticeably different cutoffs for the two compounds, while one may argue that \(q_c\) should reflect mainly the geometry of the Fermi surface and thus be practically the same in these two cases. Furthermore, the fermiology of these compounds is very complicated: in the paramagnetic state, there are 4 Fermi surfaces, two small and two large (one open and one closed). In this situation, it is hardly possible to justify any simple prescription for \(q_c\). Therefore, we have chosen a different route: we assume that \(q_c\) is the same for both materials, and choose a number which yields a good description of both the equilibrium moment in \(\text{Ni}_3\text{Al}\) and the paramagnetic susceptibility in \(\text{Ni}_3\text{Ga}\), \(q_c = 0.382 a_0^{-1}\). Note that this is larger than the diameters of the small Fermi surfaces but smaller than the radius of the Brillouin zone, \(\approx 0.5 a_0^{-1}\).

To calculate the above quantities, especially \(a, b\), we need accurate values of the velocities on a fine mesh. Numerical differentiation of energies within the tetrahedron method proved to be too noisy. Therefore we use the velocities obtained analytically as matrix elements of the momentum operator, computed within the optic program of the WIEN package. A bootstrap method [32] as described in Ref. [31], was used to obtain stable values for \(a, b\). We found for \(\text{Ni}_3\text{Al}\), using as the energy unit Ry, the length unit Bohr, and the velocity unit Ry-Bohr, \(a = 230, b = 210, v_F = 0.20, \) and \(\xi = 0.445 \mu_B\). For \(\text{Ni}_3\text{Ga}\) \(a = 140, b = 270, v_F = 0.19, \) and \(\xi = 0.556 \mu_B\). Using the resulting values of \(\xi\) each compound we obtain a magnetic moment of \(M = 0.3 \mu_B/\text{cell}\) for \(\text{Ni}_3\text{Al}\) and a paramagnetic state with the renormalized susceptibility \(\chi(0, 0) = 1/\hat{a}_2 = 6.8 \times 10^{-5} \text{emu/g}\) for \(\text{Ni}_3\text{Ga}\), thus correcting the incorrect ordering of the magnetic tendencies of these two compounds and reproducing extremely well the experimental numbers of \(M = 0.23 \mu_B, \chi(0, 0) = 6.7 \times 10^{-5} \text{emu/g}\), respectively. This qualitative behavior is due to the different coefficient \(a, i.e.,\) different \(q\) dependencies of \(\chi(0, q)\) at small \(q\), which relates to the phase space available for soft fluctuations.

Now we turn to the pressure dependence. The above results imply that beyond LDA fluctuations are already larger than the moments themselves at \(P = 0\). In this regime, we may assume that the size of the beyond LDA fluctuations is only weakly pressure dependent. Then we can apply Eq. 2 to the data shown in Fig. 3 using \(\xi = 0.47\) as needed to match the \(P = 0\) value of \(M\). This yields a value \(P_c = 10 \text{ GPa}\) in quite good agreement with the experimental value, \(P_c = 8.1 \text{ GPa}\). [7]

In conclusion, we address the LDA failure to describe the physics of magnetism in \(\text{Ni}_3\text{Al}\) and \(\text{Ni}_3\text{Ga}\) even qualitatively. We identify the problem as neglect of spin fluctuations associated with the ferromagnetic quantum critical point. These are stronger in \(\text{Ni}_3\text{Ga}\) despite the fact that the latter has a larger density of states and is therefore more magnetic in mean-field theories. The reason for the difference in the spin fluctuation spectra is in the \(q\) dependence of the non-interacting spin susceptibility.
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TABLE I. Magnetic energy (see text), magnetic moment in $\mu_B$/cell and $N(E_F)$ in eV$^{-1}$ on a per spin per formula unit basis.

|                | $|\Delta E|$ (meV) | $M$ (calc.) | $M$ (expt.) | $N(E_F)$ |
|----------------|-------------------|-------------|-------------|-----------|
| Ni$_3$Al       | 10.3              | 0.71        | 0.23        | 3.2       |
| Ni$_3$Ga       | 14.3              | 0.79        | 0.00        | 3.4       |