Why Ni_3Al Is an Itinerant Ferromagnet but Ni_3Ga Is Not

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Ni_3Al and Ni_3Ga 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_3Ga. Thus in Stoner theory it should be more magnetic, and in local-density approximation (LDA) calculations it is. However, experimentally it is a paramagnet, while Ni_3Al is an itinerant ferromagnet. We show that critical spin fluctuations are stronger in Ni_3Ga, due to weaker q dependence of the susceptibility, and this effect is enough to reverse the trend. The approach combines LDA calculations with Landau theory and the fluctuation-dissipation theorem using the same momentum cutoff 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_3Ga than in Ni_3Al.

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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 [1], e.g., the differences between UGe_2 and URhGe [2,3] and $ZrZn_2$ [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 [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_3Al and Ni_3Ga. Both of these have the ideal cubic Cu_3Au $cP4$ structure, with very similar lattice constants, $a = 3.568$ and $a = 3.576$ Å, respectively, and have been extensively studied by various experimental techniques. Ni_3Al is a weak itinerant ferromagnet, $T_c = 41.5$ K and magnetization, $M = 0.23\ \mu_B$/cell (0.077 μ_B/Ni atom) [6] with a QCP under pressure at $P_c = 8.1$ GPa [7], while Ni_3Ga is a strongly renormalized paramagnet [8]. Further, it was recently reported that Ni_3Al shows non–Fermi-liquid transport over a large range of P and T range down to very low T [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 local-density approximation (LDA) and generalized gradient approximation (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 quasiclassical 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 [10–13]—a fact that can potentially be used as a screen for materials with large fluctuation effects [14]. Previous LDA calculations showed that the magnetic tendency of both materials is overestimated within the LDA, and that Ni_3Ga is incorrectly predicted to be a ferromagnet [15–20]. Moreover, as our present results show, in the LDA the tendency to magnetism is stronger in Ni_3Ga than Ni_3Al, *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_3Ga). 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 cutoff 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_3Al.

Our LDA calculations were done using the general potential linearized augmented-plane-wave (LAPW) method with local orbital extensions [21,22] in two implementations [22–24], with the exchange-correlation functional of Hedin-Lundqvist with the von Barth–Hedin

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spin scaling. Up to 816 inequivalent **k** points were used in the self-consistent calculations, with an LAPW basis set defined by the cutoff $R_S K_{\max} = 9$, plus local orbitals to relax linearization errors. Larger numbers of **k** points between 2300 and 4060 were used in the Fermi surface integrations. The LDA electronic structure is given in Fig. 1 and Table I, 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_3Ga ($0.79\mu_B$/f.u. vs $0.71\ \mu_B$/f.u.), in agreement with other full potential calculations [19,20], and more magnetic than in earlier nonfull potential calculations [25].

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 [26] states that to the second order in the spin density the magnetic stabilization energy is expressed as $\Delta E = M^2[\int_0^M m\, dm/2\tilde{N}(m) - I/4]$, where $\tilde{N}(M)$ 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 $I_{\mathrm{Al}} = 0.385$ eV and $I_{\mathrm{Ga}} = 0.363$ eV. These give $IN(E_F) = 1.21$ and $IN(E_F) = 1.25$ for Ni_3Al and Ni_3Ga, respectively. Both numbers are larger than 1, corresponding to a ferromagnetic instability, and the value for Ni_3Ga is larger than that for Ni_3Al. Importantly, the difference comes from the density of states, since $I_{\mathrm{Al}} > I_{\mathrm{Ga}}$. 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_3Al, the critical point at $\delta a/a = -0.058$ corresponds to $P_c = 50$ GPa [27], which is much higher than the experimental value. It is interesting that, as in $ZrZn_2$ [11], the exchange splitting is very strongly **k** dependent; e.g., in Ni_3Al at some points it is as small as 40 meV/μ_B near the E_F, while at the others (of pure Ni d character) it is close to 220 meV/μ_B.

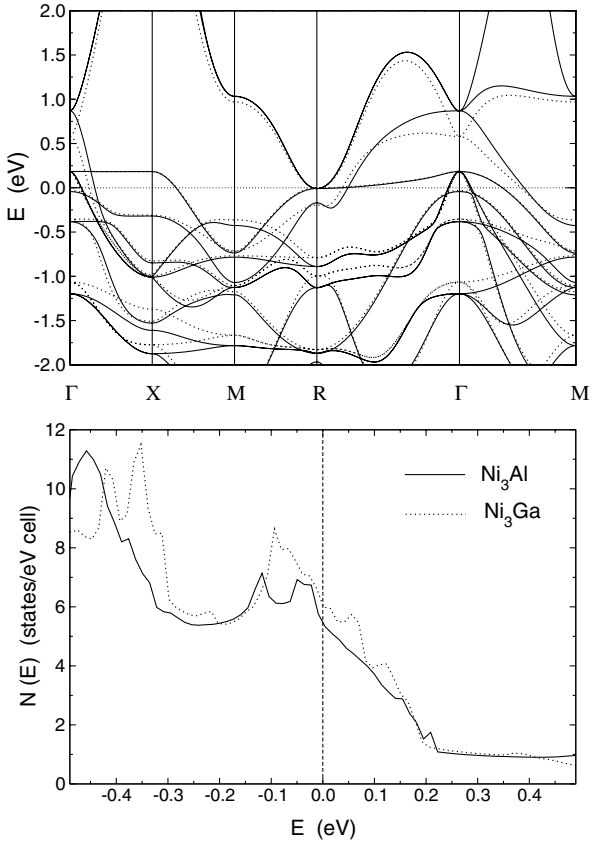

FIG. 1. Calculated LDA band structure (top) and density of states (bottom) per f.u. for non–spin-polarized Ni_3Al (solid lines) and Ni_3Ga (dotted lines). E_F is at 0 eV.

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 Γ-M or Γ-X directions is steeper in Ni_3Al (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 Γ point, 0.56 eV in Ni_3Ga and 0.85 eV in Ni_3Al. 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. Because of 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 spin orbit does not give 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

$$E(M) = a_2 M^2/2 + a_4 M^4/4 + a_6 M^6/6 + \cdots. \quad (1)$$

Treating this as a mean-field expression and adding the effects of spin fluctuations gives renormalized expansion coefficients, $\tilde{a}_i$. These are written as power series in the averaged square of the magnetic moment fluctuations beyond the LDA, ξ^2 (see Refs. [30–32]).

ξ may be estimated by requiring that the corrected Landau functional reproduces the experimental magnetic moment (for Ni_3Al) or experimental magnetic susceptibility (for Ni_3Ga). The "experimental" ξ's obtained in this manner are 0.47 and 0.55, respectively, which implies

TABLE I. Magnetic energy (see text), magnetic moment in μ_B/cell, and $N(E_F)$ in eV^{-1} on a per spin per formula unit basis.

	$\lvert\Delta E\rvert$ (meV)	M (calc.)	M (expt.)	$N(E_F)$
Ni_3Al	10.3	0.71	0.23	3.2
Ni_3Ga	14.3	0.79	0.00	3.4

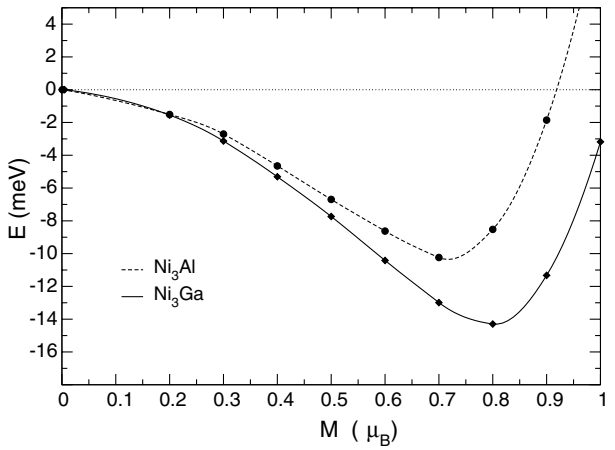

FIG. 2. Energy vs fixed spin moment for Ni_3Al and Ni_3Ga at the experimental lattice parameters. The energy zero is set to the non–spin-polarized value.

that spin fluctuation effects must be stronger in Ni_3Ga than in Ni_3Al.

We now link this with the electronic structures. A standard formula for estimating ξ^2 comes from the fluctuation-dissipation theorem [33], which yields

$$\xi^2 = (2\hbar/\Omega)\int d^3q \int (d\omega/2\pi)\mathrm{Im}\chi(\mathbf{q}, \omega). \quad (2)$$

Here Ω is the Brillouin zone volume and χ the magnetic susceptibility. Using the lowest order expansion for χ,

$$\chi_0(\mathbf{q}, \omega) = N(E_F) - aq^2 + ib\omega/q, \quad (3)$$

$$\chi^{-1}(\mathbf{q}, \omega) = \chi_0^{-1}(\mathbf{q}, \omega) - I, \quad (4)$$

where $\chi_0(\mathbf{q}, \omega)$ is the noninteracting susceptibility, one can derive a formula for ξ^2 [30,33], whose coefficients can be related to the electronic structure [31–33]. Formally, ξ describes not all spin fluctuations, but just those long-range, low-frequency fluctuations that are not included in the LDA. So ideally the integrand in Eq. (2) is not the observable susceptibility, but the difference between that and the one of the reference system far from the QCP. This is discussed in more detail in Ref. [32] where, among other things, possible ways to identify a suitable reference system are described. However, here we resort to a conventional prescription [30,33] that uses a q-dependent frequency cutoff $\omega_c(q) = v_F q$ (the Landau damping threshold), and an unknown momentum cutoff q_c, which is usually assumed to be related to the Fermi surface geometry (and thus likely to be the same in both Ni_3Al and Ni_3Ga) I.e., it is assumed that all fluctuations with $\omega > \omega_c$ and $q > q_c$ are in the LDA. The final result reads [30,33]

$$\xi^2 = \frac{b v_F^2 N(E_F)^2}{2a^2\Omega}[Q^4 \ln(1 + Q^{-4}) + \ln(1 + Q^4)], \quad (5)$$

where $a = (d^2\langle N(E_F)v_x^2\rangle/dE_F^2)/12$, $b = \langle N(E_F)v^{-1}\rangle/2$, $v_F = \sqrt{3(d^2\langle N(E_F)v_x^2\rangle}$, $Q = q_c\sqrt{a/bv_F}$, and q_c is the cutoff parameter for integration in Eq. (2). 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 (3) 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 four 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 Ni_3Al and the paramagnetic susceptibility in Ni_3Ga, $q_c = 0.382\, a_0^{-1}$. Note that this is larger that the diameters of the small Fermi surfaces but smaller than the radius of the Brillouin zone, $\approx 0.5\, a_0^{-1}$.

For these quantities, especially a, we need accurate velocities on a fine mesh. Numerical differentiation of energies in the tetrahedron method proved to be too noisy. So we used the velocities obtained analytically as matrix elements of the momentum operator, computed within the *optic* program of the WIEN package. A bootstrap method [34], as in Ref. [31], was used to obtain stable values for a, b. For Ni_3Al (energy in Ry, length in Bohr, and velocity in Ry · Bohr) $a = 230$, $b = 210$, $v_F = 0.20$, and $\xi = 0.445\ \mu_B$. For Ni_3Ga $a = 140$, $b = 270$, $v_F = 0.19$, and $\xi = 0.556\ \mu_B$. Using the resulting ξ for each compound we get $M = 0.3\mu_B$/cell for Ni_3Al and a paramagnetic state with $\chi(0, 0) = 1/\tilde{a}_2 = 6.8 \times 10^{-5}$ emu/g for Ni_3Ga, thus correcting the ordering of the magnetic tendencies of these two compounds and reproducing extremely well the experimental $M = 0.23\ \mu_B$ and $\chi(0, 0) = 6.7 \times 10^{-5}$ emu/g, respectively. This comes from the different values of a, i.e., different q dependencies of $\chi_0(q, 0)$ at small q, which relates to the phase space available for soft fluctuations [35].

While, as mentioned, the integrand in Eq. (2) is not exactly the observable susceptibility, it is instructive to compare with neutron scattering data [36]. In our calculations the ratio of the coefficients a for Ni_3Ga and Ni_3Al is 1.65, rather close to the ratio of the corresponding coefficients (c, in their notation) in Refs. [36].

Regarding the pressure dependence, the above results imply that beyond LDA fluctuations are already larger

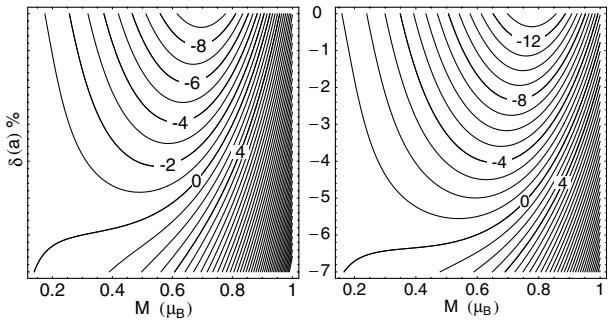

FIG. 3. FSM calculations for Ni_3Al (left) and Ni_3Ga (right) under hydrostatic pressures. Magnetic energy (energy relative to the non–spin-polarized result at the same volume) as a function of the moment and linear compression.

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 the same formalism 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 $P_c = 10$ GPa in quite good agreement with the experimental value, $P_c = 8.1$ GPa [7].

In conclusion, we address the LDA failure to describe the physics of magnetism in Ni_3Al and Ni_3Ga even qualitatively. We identify the problem as neglect of spin fluctuations associated with the ferromagnetic quantum critical point. These are stronger in Ni_3Ga 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 noninteracting spin susceptibility.

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[1] R. B. Laughlin *et al.*, Adv. Phys. **50**, 361 (2001).
[2] S. S. Saxena *et al.*, Nature (London) **406**, 587 (2000).
[3] D. Aoki *et al.*, Nature (London) **413**, 613 (2001).
[4] C. Pfleiderer *et al.*, Nature (London) **412**, 58 (2001).
[5] C. P. Pfleiderer, S. R. Julian, and G. G. Lonzarich, Nature (London) **414**, 427 (2001).
[6] F. R. de Boer *et al.*, J. Appl. Phys. **40**, 1049 (1969).
[7] P. G. Niklowitz, F. Beckers, N. Bernhoeft, D. Braithwaite, G. Knebel, B. Salce, J. Thomasson, J. Floquet, and G. G. Lonzarich (unpublished); in Proceedings of the Conference on Quantum Complexities in Condensed Matter, 2003.
[8] S. M. Hayden, G. G. Lonzarich, and H. L. Skriver, Phys. Rev. B **33**, 4977 (1986).
[9] M. J. Steiner *et al.*, Physica B (Amsterdam) **329**, 1079 (2003).
[10] D. J. Singh and I. I. Mazin, Phys. Rev. B **63**, 165101 (2001).
[11] D. J. Singh and I. I. Mazin, Phys. Rev. Lett. **88**, 187004 (2002).
[12] A. Aguayo and D. J. Singh, Phys. Rev. B **66**, 020401 (2002).
[13] D. J. Singh, Phys. Rev. B **68**, 020503 (2003).
[14] This is distinct from the well-known problems that the LDA has in systems with strong Hubbard correlations, so such a signature should not be interpreted as evidence of strong Hubbard correlations.
[15] J. J. Buiting, J. Klübler, and F. M. Mueller, J. Phys. F **13**, L179 (1983).
[16] V. L. Moruzzi and P. M. Marcus, Phys. Rev. B **42**, 5539 (1990).
[17] B. I. Min, A. J. Freeman, and H. J. F. Jansen, Phys. Rev. B **37**, 6757 (1988).
[18] J. H. Xu *et al.*, Phys. Rev. B **41**, 5010 (1990).
[19] G. Y Guo, Y. K. Wang, and Li-Shing Hsu, J. Magn. Magn. Mater. **239**, 91 (2002).
[20] L.-S. Hsu, Y.-K. Wang, and G. Y. Guo, J. Appl. Phys. **92**, 1419 (2002).
[21] D. J. Singh, *Planewaves Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994).
[22] D. Singh, Phys. Rev. B **43**, 6388 (1991).
[23] S. H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).
[24] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for for Calculating Crystal Properties* (Techn. Universitat Wien, Austria, 2001), ISBN 3-9501031-1-2.
[25] H. Winter, Z. Szotek, and W. M. Temmerman, Solid State Commun. **74**, 547 (1990).
[26] G. L. Krasko, Phys. Rev. B, **36**, 8565 (1987).
[27] We used $P = B/B'[(V/V_0)^{B'} - 1]$. V/V_0 is the volume compression. B and B' are the bulk modulus and derivative. We used the experimental $B = 174$ GPa for Ni_3Al [28], which agrees with the experimental volume LDA value [29]. We used the calculated value $B' = 5.2$.
[28] F. Wallow, G. Neite, W. Schroer, and E. Nembach, Phys. Status Solidi A **99**, 483 (1987).
[29] J. E. Osburn, M. J. Mehl, and B. M. Klein, Phys. Rev. B **43**, 1805 (1991).
[30] M. Shimizu, Rep. Prog. Phys. **44**, 329 (1981).
[31] P. Larson, I. I. Mazin, and D. J. Singh, Phys. Rev. B **69**, 064429 (2004).
[32] I. I. Mazin, D. J. Singh, and A. Aguayo, cond-mat/0401563.
[33] T. Moriya and A. Kawabata, J. Phys. Soc. Jpn. **34**, 639 (1973).
[34] B. Efron and R. J. Tibshirani, *An Introduction to the Bootstrap* (Chapmann and Hall, New York, 1993).
[35] Correspondingly, these calculations predict a stronger effect of spin fluctuations in Ni_3Ga than in Ni_3Al, but whether this will be enough to reverse the trend observed in the uncorrected calculations depends on the choice of q_c. However, for all reasonable choices of $q_c \gtrsim 2k_F$ the reversal takes place.
[36] N. R. Bernhoeft *et al.*, Phys. Rev. B **28**, 422 (1983); Phys. Rev. Lett. **62**, 657 (1989).