Interplay between Disorder and Quantum and Thermal Fluctuations in Ferromagnetic Alloys: The case of $UCu_2Si_{2-x}Ge_x$

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We consider, theoretically and experimentally, the effects of structural disorder, quantum fluctuations, and thermal fluctuations in the magnetic and transport properties of certain ferromagnetic alloys. We study the particular case of $UCu_2Si_{2-x}Ge_x$. The low temperature resistivity, $\rho(T, x)$, exhibits Fermi liquid behavior as a function of temperature T for all values of x, which can be interpreted as a result of the magnetic scattering of the conduction electrons from the localized U spins. The residual resistivity, $\rho(0, x)$, follows the behavior of a disordered binary alloy. The observed nonmonotonic dependence of the Curie temperature, $T_c(x)$, with x can be explained within a model of localized spins interacting with an electronic bath. Our results clearly show that the Curie temperature of certain alloys can be enhanced due to the interplay between quantum and thermal fluctuations with disorder.

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Ternary intermetallic alloys of the type MT_2X_2, where M is an actinide or rare earth element, T is a transition metal, and X is Si or Ge, have been a subject of intense experimental and also theoretical interest due to their interesting magnetic and transport properties [1]. In these systems, M is usually a magnetic atom with a partially filled f shell, such as U or Ce, and the conduction takes place in the d bands of the transition metal such as Cu. These materials crystallize in the $ThCr_2Si_2$ tetragonal structure, with the $I4/mmm$ space group, and exhibit a rich variety of ground states [2]. For example, while UCu_2Si_2 is a collinear ferromagnet with a high Curie temperature ($\sim$100 K) [1], URu_2Si_2 behaves similar to an Ising antiferromagnet [3], with strong crystalline fields [4], a low Néel temperature, and an anomalously small low temperature effective moment. Moreover, while the former is an ordinary metal at low temperatures, the latter is a superconductor. More generally, it has been noticed that both the magnetic and transport properties of such systems can be *classified* with respect to the smallest distance between two M atoms, a phenomenological parameter, d_h, called the *Hill* distance [5,6]. However, a theoretical explanation for the wealth of behavior observed in these materials is still lacking.

In recent years, the interest in controlling the Curie temperature of diluted magnetic semiconductors (DMS) such as $Ga_{1-x}Mn_xAs$ has renewed the interest in the nature of ferromagnetism in disordered alloys [7]. However, DMS have many complications associated with the fact that the magnetic atom is also a donor/acceptor and its location is random in the lattice, leading to strong magnetic as well as structural disorder. Therefore, theoretical approaches to DMS are bound to be rather complex. In this work we follow a different route. We would like to separate the different physical mechanisms that control ferromagnetism in alloys. In $UCu_2Si_{2-x}Ge_x$, the magnetic sublattice is not directly affected by disorder which occurs only on the deep p orbitals of Si/Ge. This structural disorder, however, affects the conduction band because of the $p-d$ hybridization. Furthermore, because Si and Ge are isovalent there is no affect on the carrier density. Therefore, this class of ferromagnetic materials allows the detailed study of the effect of structural disorder on the ferromagnetic properties without introducing extra complications. As we shall see, even this simplified problem has already unexpected behavior due to the interplay between structural disorder and quantum or thermal fluctuations [8]. In particular, we show that the unusual nonmonotonic behavior of $T_c(x)$ as a function of x can be understood as a crossover between ballistic and diffusive electronic behavior. Therefore, one can show that, by controlling the amount of disorder in the sample, one can control directly the Curie temperature of the material. The repercussion of these results on DMS is obvious.

The $UCu_2Si_{2-x}Ge_x$ alloys produced for this study were stoichiometrically weighed and melted together in a zirconium-gettered purified argon atmosphere. The polycrystalline samples were wrapped in tantalum foil and annealed in sealed quartz glass tubes to ensure good crystalline order. The tetragonal structure of the polycrystalline samples was checked by x-ray powder diffraction at room temperature. We found that annealing at 875 °C for two weeks gave the best results (minimal weight loss and sharpest magnetic transitions). The samples were cut into rectangular bars [$(0.8 \times 0.8 \times 8)\ \mathrm{mm}^3$] for resistance measurements. Platinum wires were spot welded to these samples. Electrical measurements used standard four-wire dc techniques. The

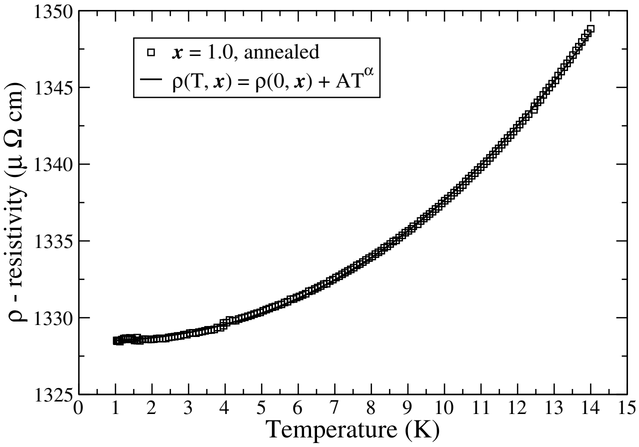

FIG. 1. Resistivity of $UCu_2Si_{2-x}Ge_x$ as a function of temperature for $x = 1.0$. For the fit we used $\alpha = 2.33$. Similar behavior for the resistivity is observed in all the other annealed samples where α did not significantly deviate from the FL value $\alpha = 2$.

relative accuracy of the resistance measurements was approximately 4%. Measurements of susceptibility were performed using a SQUID susceptometer in a field $B_0 = 1000$ G.

The two electrons on the f level of U^{4+}, which is assumed to be the configuration of the U atoms in the compound, are likely to be found in the $^3H_4$ Hund's multiplet configuration. The corresponding effective moment is $\mu_{\mathrm{eff}} = 3.58\mu_B$ in agreement with the measured moment at high temperatures in UCu_2Si_2 [1]. Magnetic susceptibility, $\chi(T)$, measurements also suggest a small crystal field splitting at low temperatures which will be neglected in what follows. In UCu_2Ge_2, on the other hand, the measured effective moment is $\mu_{\mathrm{eff}} = 2.40\mu_B$ [1], which might be due to either crystal field effects or magnetic moment compensation (it may also be related to the antiferromagnetic transition observed at $T_N \sim 40$ K).

The resistivity data suggest that the main scattering mechanism at low temperatures is of magnetic origin, with the conduction electrons being scattered by magnetic excitations [9] and has the FL form: $\rho(T, x) = \rho(0, x) + AT^{\alpha}$, with $\alpha \approx 2$ (see Fig. 1). $\rho(0, x)$ for a random binary alloy is expected to have the functional form: $\rho(0, x) = \rho_{\mathrm{Si}}(2 - x)/2 + \rho_{\mathrm{Ge}}x/2 + \bar{\rho}x(2 - x)$, where ρ_{Si} (ρ_{Ge}) is the intrinsic resistivity of the pure compound at $x = 0$ ($x = 2$), and the last term is the contribution from Nordheim's rule [10]. However, we have found that the experimental value of $\rho(0, x)$ does not follow this functional dependence with x. The reason for this discrepancy is the existence of microcracks in the sample due to internal stresses generated by doping. In order to eliminate their effect from the data, we normalize $\rho(0, x)$ by the high temperature resistivity, $\rho(300\ \mathrm{K}, x)$. In Fig. 2, we show $\rho(0, x)/\rho(300\ \mathrm{K}, x)$ as a function of x together with the theoretical result with the above x dependence. The experimental data, plotted in this way, are very well described by the random alloy expression.

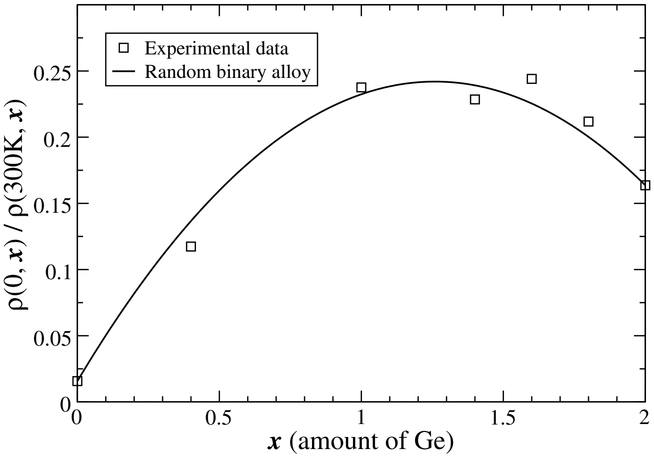

FIG. 2. Experimental data for the residual resistivity of $UCu_2Si_{2-x}Ge_x$ normalized by its value at 300 K (squares) and the fit corresponding to the binary alloy (solid line), according to the text.

$T_c(x)$ was obtained from susceptibility measurements and a nonmonotonic behavior as a function of x was observed (see Fig. 3). A monotonic increase in T_c is naively expected having in mind that the magnetic interaction in this system is RKKY and there is a shift of the Fermi energy due to the change in the volume of the unit cell with x (see below). However, the unexpected nonmonotonicity in $T_c(x)$ was predicted recently by two of us (M. B. S. N. and A. H. C. N.) due to the interplay between fluctuations and structural disorder in alloys [8]. The origin of such behavior can be tracked down to a change on the transport properties from ballistic (clean) to diffusive (dirty), depending on x.

The physical properties of the two stoichiometric samples, UCu_2Si_2 and UCu_2Ge_2, are shown in Table I.

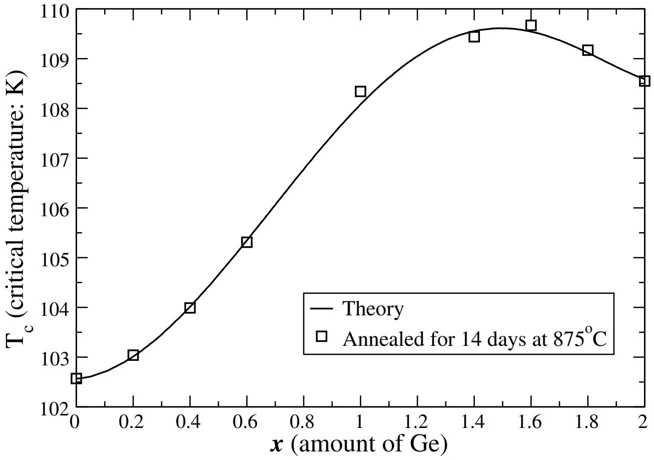

FIG. 3. Curie temperature, T_c, as a function of the amount of Ge, x. Experimental results: squares; theoretical result from Eq. (3): solid line.

TABLE I. Lattice parameters a and c of the tetragonal structure $ThCr_2Si_2$ measured by x-ray powder diffraction; effective moment μ_{exp} determined out of $\chi(T)$ for $T > 200$ K [1]; Fermi energy E_F estimated by band structure calculations and measured from the bottom of the Cu d band; ferromagnetic transition temperature T_c determined from susceptibility measurements in a field $B_0 = 1000$ G.

	a [Å]	c [Å]	$\mu^J_{\mathrm{eff}}[\mu_B]$	$\mu_{\mathrm{exp}}[\mu_B]$	E_F [eV]	T_c [K]
UCu_2Si_2	3.981	9.939	3.58	3.58	5.95	102.5
UCu_2Ge_2	4.063	10.229	3.58	2.40	5.61	108.55

The magnetic exchange interaction between U spins is ascribed to an isotropic RKKY interaction. Such interaction has already been shown to capture correctly the physics of these two compounds as well as of other isostructural systems such as URh_2Si_2 and UPd_2Si_2 [1]. Moreover, band structure calculations [11] show a parabolic dispersion for the Cu d band, at least along the direction of the tetragonal axis in the Brillouin zone. Assuming that alloying only introduces scattering centers for the conduction electrons, we propose the following Hamiltonian for these systems:

$$\begin{aligned}\mathcal{H} &= \sum_{\mathbf{k},\sigma}\varepsilon_d(\mathbf{k})d^\dagger_{\mathbf{k},\sigma}d_{\mathbf{k},\sigma} + \sum_{\mathbf{k},\mathbf{k}'\sigma,\sigma'} V_{\mathbf{k},\mathbf{k}'}d^\dagger_{\mathbf{k},\sigma}d_{\mathbf{k}',\sigma'} \\ &\quad + \sum_{\mathbf{k},\mathbf{k}'\sigma,\sigma'} \mathcal{J}(\mathbf{k})\mathbf{J}_{-\mathbf{k}} \cdot d^\dagger_{\mathbf{k}',\sigma}\vec{\sigma}_{\sigma\sigma'}d_{\mathbf{k}'+\mathbf{k},\sigma'} \\ &\quad + U_c\sum_{\mathbf{q}}\rho_{\mathbf{q}}\rho_{-\mathbf{q}}, \end{aligned} \tag{1}$$

where $\mathcal{J}(\mathbf{r}_i - \mathbf{r}_j) = \sum_{\mathbf{k}}\mathcal{J}(\mathbf{k})e^{\mathrm{i}\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}$ is an effective exchange coupling due to the hybridization between the f states and conduction electrons, $d^\dagger_{i,\sigma}$ ($d_{i,\sigma}$) is the conduction electron creation (annihilation) operator for an electron with spin $\sigma = \uparrow, \downarrow$ on the ith site, $\mathbf{J}_i = \sum_{\mathbf{k}}\mathbf{J}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}_i}$ is the U magnetic moment on the ith site, $\vec{\sigma}_{\sigma\sigma'}$ are the Pauli matrices, $\varepsilon_d(\mathbf{k})$ is dispersion of the conduction band, $V_{\mathbf{k},\mathbf{k}'}$ is a random impurity scattering potential, and U_c is the Coulomb interaction between the conduction electrons ($\rho_{\mathbf{q}} = \sum_{\mathbf{k},\sigma}c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c_{\mathbf{k},\sigma}$ is the density operator). The introduction of electron-electron interactions in the conduction band is important because of the enhancement of the magnetic interactions due to the magnetic polarizability of the conduction band [12]. Furthermore, although (1) also describes the Kondo effect between the U spin and the conduction band, the Kondo effect does not play any role in the ferromagnetic phase [13]. The above Hamiltonian (1) can be derived from a more general three band Hamiltonian that includes not only the conduction electron d band and f states but also the p band of Si/Ge with a random distribution of on-site energies [14].

As a first approach, we can perform a simple calculation in order to estimate $T_c(x)$ within a Weiss mean field theory of the Hamiltonian (1) with $U_c = V = 0$. We find (we use units where $\hbar = k_B = 1$)

$$T_c^{\mathrm{MF}} = \frac{J(J+1)}{8}\frac{\mathcal{J}^2}{E_F}\frac{N_eN_m}{N_A^2}, \tag{2}$$

where N_e, N_m, and N_A are, respectively, the number of conduction electrons, magnetic ions, and total number of atoms, per unit cell, and E_F is the Fermi energy. According to (2), the ratio between the Curie temperatures for the two stoichiometric samples, $T_c(x=2)/T_c(x=0)$, depends only on the ratio $\mathcal{J}^2/E_F$. From band structure calculations, we estimate $E_F(x=0) = 5.95$ eV and $E_F(x=2) = 5.61$ eV, both measured with respect to the bottom of the Cu d band. If we make the further assumption that $\mathcal{J}$ is not changed with x, we conclude that $T_c(x=2)/T_c(x=0) = E_F(x=0)/E_F(x=2)$ is fairly satisfied with the values of Table I. This simple formulation of the problem, however, is not capable of explaining the nonmonotonic behavior of $T_c(x)$ as shown in Fig. 3.

In a previous theoretical work [8], it was shown that a continuum SU(N) formulation of the effective Heisenberg Hamiltonian, obtained after integration of the conduction electrons in (1), that takes into account both the spin fluctuations and dissipation introduced by the electronic bath, might be a reasonable starting point to explain Fig. 3. In that formulation, the Curie temperature T_c can be determined from the equation [8]

$$\frac{1}{g_0} = \int\frac{d^3\mathbf{k}}{(2\pi)^3}\int_{-\Omega_k^0}^{\Omega_k^0}\frac{d\omega}{\pi}\frac{k\gamma_0(kl)\omega n_B(\omega/T_c)}{[k(k^2-c_0\omega)]^2+[\gamma_0(kl)\ \omega]^2}, \tag{3}$$

where $n_B(z) = (e^z - 1)^{-1}$ is the Bose-Einstein distribution function, $\Omega_k^0 = (2k_F)^2k/\gamma_0(kl)$ is an energy cutoff, $g_0 = Na/2\mathcal{J}_HJ^2$ is the coupling constant, $c_0 = 1/\mathcal{J}_HJa^2$ is the topological constant, and we have defined $\mathcal{J}_H = \mathcal{J}^2(k_Fa)^3/4\pi^2E_F[1 - a^3N(0)U_c]$ which plays the role of the effective exchange. Furthermore, $N(0) = m^*k_F/\pi^2$ is the density of states at the Fermi energy $E_F = k_F^2/2m^*$, $k_F = (3\pi^2n)^{1/3}$ is the Fermi wave vector, and $n = N_e/a^3$ is the electronic density per unit cell with lattice spacing a. Finally, the dissipation coefficient is given by [15]

$$\gamma_0(kl) = \frac{8k_F^2}{v_F[1-a^3N(0)U_c]}\frac{\arctan(kl)}{1-(kl)^{-1}\arctan(kl)}, \tag{4}$$

where l is the electronic mean-free path, and $v_F = k_F/m^*$ is the Fermi velocity.

Equation (3) relates T_c to a number of material properties and reduces to Eq. (2) in the limit of $\gamma_0 \to 0$ and $J \to \infty$ [14]. Each Cu^{2+} contributes one electron to the conduction band and we can set $N_e = 8$. The replacement of Si by Ge alters the size of the unit cell; thus, we use Vegard's law to write $a = a_{\mathrm{Si}}(2-x)/2 + a_{\mathrm{Ge}}x/2$, where $a_{\mathrm{Si}} = 5.4$ Å and $a_{\mathrm{Ge}} = 5.527$ Å were chosen in order to reproduce the volume of the unit cell (see Table I). Notice that the product k_Fa does not depend on x. We also fix the values of $m^*_{\rm Si}$ and $m^*_{\rm Ge}$ so that the calculated E_F matches the values obtained from band structure calculations, and we use $J = 4$, $N = 2$, and $U_c = 0.45$ eV, consistent with estimates from Thomas-Fermi theory [14].

The electronic mean-free path can be obtained from the Drude relation: $\rho = m^* v_F/ne^2 l$ (e is the charge of the electron). From the residual resistivity (see Fig. 2), we obtain the dependence of l on x [14]. Typical values for the product $k_F l$ range from $k_F l \sim 10$ for $x = 0$, where the system is in the ballistic regime [note that $\gamma_0(k_F l \gg 1) \propto$ const], to $k_F l \sim 0.74$ for $x = 1.3$, in the diffusive regime [$\gamma_0(k_F l \ll 1) \propto 1/k_F l$]. In particular, $k_F l \simeq 0.8$ for $x = 1.6$, where T_c is the highest [14]. Notice also that the maximum in $T_c(x)$ in Fig. 3 is very close to the position where the resistivity (mean-free path) is largest (shortest) in Fig. 2 indicating that T_c is mostly controlled by electron scattering. Thus, as discussed in [8], since T_c of a dissipative spin fluctuation system is larger in the diffusive relative to the ballistic regime, we can understand the nonmonotonic behavior of $T_c(x)$ in Fig. 3 as a direct consequence of the behavior of the residual resistivity in Fig. 2. An enhancement of the Curie temperature in the disordered single band Hubbard model has also been reported recently in Ref. [16].

Finally, because of the changes in the unit cell volume, we expect $\mathcal{J}(x)$ to be monotonically decreasing with x [14]. For the stoichiometric samples, $\rm UCu_2Si_2$ and $\rm UCu_2Ge_2$, $\mathcal{J}$ can be estimated from a hybridization model for the magnetic-ordering behavior in U intermetallic compounds such as the one considered here [17]. According to Ref. [17], the hybridization is governed by the f-d hybridization, V_{fd}, the strength of which is a function of the ionic radius of $\rm U^{4+}$ and $\rm Cu^{2+}$, their angular momentum quantum numbers, l and m, and their relative distance in the unit cell. The exchange parameter, $\mathcal{J}$, is then calculated from V_{fd} by means of a Schrieffer-Wolf transformation [17]. Typical values found for $\mathcal{J}$ are between 8 meV ($x = 0$) and 3.5 meV ($x = 2$). For $0 < x < 2$, however, the situation is much more complex due to the effects of disorder in the hybridization matrix elements. Nevertheless, we find that $\mathcal{J}$ is a monotonically decreasing function of x so that all the nonmonotonicity in $T_c(x)$ can be uniquely attributed to the disorder introduced by the conduction electron scattering potential. The final theoretical value of $T_c(x)$, from Eq. (3), is shown as the continuous line on Fig. 3.

In conclusion, we have studied, theoretically and experimentally, the effect of structural disorder in the magnetic and transport properties of ferromagnetic alloys of the form $\rm UCu_2Si_{2-x}Ge_x$. We have shown that the interplay between disorder and magnetism leads to an unexpected nonmonotonic behavior of the Curie temperature that cannot be explained by naive mean field theories. We have shown that, in order to describe the ferromagnetic ordering in these systems, one needs to take into account the dissipation introduced by the coupling of the local spins to the electronic heat bath. Dissipation is controlled by the electron mean-free path and therefore is sensitive to the amount of disorder and the electron-electron interactions. The same physical processes can be important in the physics of DMS. However, the introduction of magnetic disorder is very important and has to be carefully considered.

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