Mean-field heat capacity of dilute magnetic alloys

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Abstract

Using an asymptotic solution of the \( M \)-impurity thermodynamics of a dilute s-d system, the impurity energy and impurity heat capacity \( \Delta C(T) \) are derived for dilute magnetic alloys with spin 1/2 and spin 3/2 impurities. The parameters which enter \( \Delta C \) are adjusted to fit experimental data on impurity heat capacity of CuCr and \((La_{1-x}Ce_x)Al_2\). Agreement is satisfactory for CuCr, at temperatures below 1K, and good for \((La_{1-x}Ce_x)Al_2\). The magnitude of theoretical \( \Delta C(T) \) agrees with experiment and does not require scaling as in previous s-d theories. Nonlinear dependence of \( \Delta C(T) \) on impurity concentration has been accounted for the first time.

1 Introduction

Existing theories of anomalous thermal behaviour of dilute magnetic alloys (DMA) (e.g. Refs. [1, 2, 3, 4, 5, 6, 7, 8, 9]) have provided only partial quantitative explanation of these anomalies. Most of these investigations were restricted to an s-d system consisting of a single magnetic impurity interacting with the electron gas.

Significant progress was made by Andrei et al. [4, 5], who solved the s-d thermodynamics for an s-d system with impurities treated as indistinguishable particles. Their heat capacity and magnetization curves, after scaling by an adjusted factor, provide a good fit to experimental data on \((La_{1-x}Ce_x)Al_2\).

The disadvantage of almost all existing theories of DMA is linear dependence of resulting thermodynamic functions on impurity concentration \( c \). The dependence of DMA experimental data on \( c \) is more complex, e.g. the temperature at which DMA resistivity minimum occurs is proportional to \( c^{1/5} \) [1] and normalized DMA impurity heat capacity \( \Delta C/c \) is not constant in \( c \) [10].
A different approach to the thermodynamics of DMA, in which the thermodynamic functions do not require rescaling and depend on \( c \) nonlinearly, was proposed by the author in Ref. [11]. The starting point in this approach is the first quantization s-d Hamiltonian \( H_1^{(n,M)} \) describing \( n \) electrons and \( M \) distinguishable, arbitrarily positioned impurities with single-component spins interacting via a locally smeared s-d interaction \( U(\vec{R}_\alpha - \vec{r}_i)S_{\alpha \sigma z_i} \):

\[
H_1^{(n,M)} = A^{(n)} \left( H_0^{(n)} + g^2 \sum_{\alpha=1}^{M} \sum_{i=1}^{n} U(\vec{R}_\alpha - \vec{r}_i)S_{\alpha \sigma z_i} \right),
\]

where \( A^{(n)} \) denotes the antisymmetrizer with respect to electron variables with indices \( i = 1, \ldots, n \),

\[
H_0^{(n)} = -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \Delta_i.
\]

\( \vec{R}_\alpha \) denotes the position of \( \alpha \)th impurity, \( S_{\alpha \sigma z} \) its spin operator and \( \vec{r}_i, \sigma z_i \) the corresponding quantities of the \( i \)th electron. The considerations of Ref. [11] remain valid for any sufficiently regular function \( U \) depending on \( |\vec{R}_\alpha - \vec{r}_i| \).

It was shown in Ref. [11], that in the dilute limit of small \( c \) (d-lim) the s-d interaction is separable and the system’s free energy per electron \( f(H_1^{(n,M)}, \beta) \) is equal asymptotically to that of \( n \) noninteracting electrons with the 1-electron Hamiltonian

\[
h_{0}^{(1,M)}(\xi, \eta) = h_{0}^{(1,M)}(\xi, \eta) + \frac{1}{2}M(\xi^2 - \eta^2)\mathbb{I},
\]

where

\[
h_{0}^{(1,M)}(\xi, \eta) = h_{0}^{(1)}(\xi) - g\sqrt{n}(\xi - \eta) \sum_{\alpha=1}^{M} U_{\alpha}^{(1)} \sigma_{z}^{(1)}
\]

(3b)

and \( M \) impurities described by the Hamiltonian

\[
h_{\text{imp}}^{(M)}(\xi) = g\sqrt{n} \sum_{\alpha=1}^{M} S_{z\alpha} + \frac{1}{2}g^2 \sum_{\alpha=1}^{M} S_{z\alpha}^2.
\]

(4)

\( U_{\alpha}^{(1)} \) in Eq. (3b) is the multiplication operator by \( U(\vec{R}_\alpha - \vec{r}_i) \) and \( \eta(\xi) = \xi - f_2(\xi), \) with

\[
f_2(\xi) = -\frac{g}{\sqrt{n}} \langle S_z \rangle_{h_{\text{imp}}^{(1)}}, \quad \langle B \rangle_h := \frac{\text{Tr}(B e^{-\beta h})}{\text{Tr} e^{-\beta h}},
\]

(5)

whereas \( \xi \) is the solution of the equation

\[
\xi = f_1(f_2(\xi)) + f_2(\xi)
\]

(6)

with

\[
f_1(\xi) = g\sqrt{n} \langle \Gamma_1 U_{\alpha}^{(1)} \sigma_{z}^{(1)} \rangle_{\alpha} \Gamma_1^{\alpha} \langle \tilde{K}_{\text{imp}}^{(1,M)}(\xi,0) \rangle,
\]

(7)

\[
\Gamma_1^{n} B^{(1)} := A^{(n)} \left( B^{(1)} \otimes \mathbb{I}^{(n-1)} \right) A^{(n)},
\]

(8)
which minimizes the mean-field free energy per electron $f(h^{(n,M)}, \beta)$, where

$$h^{(n,M)}(\xi, \eta) = h^{(n,M)}_c(\xi, \eta) + h^{(M)}_{\text{imp}}(\xi).$$  \hfill (8)

Asymptotic equivalence of $H^{(n,M)}_1$ and $h^{(n,M)}$ is expressed by the equality

$$\lim_{n \to \infty} d\lim f(H^{(n,M)}_1, \beta) = \lim_{n \to \infty} d\lim f(h^{(n,M)}, \beta) = \lim_{n \to \infty} f(A^{(n)}H_0^{(n)}, \beta).$$  \hfill (9)

The question arises, to what extent is the mean-field s-d Hamiltonian $h^{(n,M)}$ capable of providing a reliable theory of DMA thermal behaviour. Here a partial answer to this question is found by showing that impurity heat capacity curves of two CuCr alloys [10] with $c = 21.7$ ppm, 51 ppm and (La$_{1-x}$Ce$_x$)Al$_2$ [12] with $x = 0.0064$ can be satisfactorily explained in terms of $h^{(n,M)}$ thermodynamics.

To this end, the 1-particle equilibrium density operator $\rho^{(1)}$ of a quantum gas, in a field of randomly positioned wells, is first analysed in Section 2. Such operator appears, e.g. in the equation for the fugacity $z$:

$$\text{Tr} z^\rho^{(1)} \left( \mathbb{1} + z^\rho^{(1)} \right)^{-1} = n$$  \hfill (10)

where

$$\rho^{(1)} := \exp \left[ -\beta h^{(1,M)}_c(\xi, 0) \right]$$

It is shown that, in the low-temperature régime, such a gas behaves effectively like a system of free particles at a temperature higher than that of the real system.

In Section 3 the mean-field impurity energy $\Delta U_{s-d}$ of the s-d system, relative to that of the free electron gas, is derived for impurity spins 1/2, 3/2. Here the crucial question is the form of $f_1$. An approximate Sommerfeld-type expansion of $f_1(\xi)$ is found, which is subsequently applied in the simplest truncated form, viz., $f_1(\xi) = b_0 + b_1\xi$, with $b_0, b_1 \in \mathbb{R}^1$. As a consequence, $\Delta U_{s-d}$ depends on five parameters: $b_0, b_1, g, M, \Delta T$, $M$ denoting the number of impurities in the considered s-d subsystem of the molar s-d system and $\Delta T > 0$ the shift in temperature scale due to random interactions unaccounted for by the s-d Hamiltonian [11].

The expression for the mean-field heat capacity

$$\Delta C(T) = \frac{d\Delta U_{s-d}}{dT}$$  \hfill (11)

was calculated analytically and the parameters $b_0, b_1, g, M, \Delta T$ adjusted to obtain directly the best possible fit of mean-field $\Delta C(T)/c$ with experimental data, without additional rescaling procedures.

Variation of $\Delta C/c$ with $c$ [10] requires different values of $b_0, b_1, g, M, \Delta T$ for different impurity concentrations. In this manner, for the first time, nonlinearity of $\Delta C(T)/c$ with respect to $c$ has been accounted for.
2 1-particle density operator of a quantum gas in a field of randomly positioned wells

The Hamiltonian $H^{(n,M)}_1$ gives only a simplified account of the interactions present in an s-d system. It does not contain terms representing the Coulomb interactions between electrons and the screened Coulomb pseudo-potential $\sum_\alpha U_C(\alpha)$ of each electron in the field of impurities. In order to investigate the effect of such potential on the electron gas in a DMA, let us examine the 1-particle density operator of a gas of negatively charged particles interacting with randomly positioned positively charged ions in a region $\Lambda$.

Let

$$h^{(1)} = -\frac{\hbar^2}{2m} \Delta + \sum_\alpha U^{(1)}_C$$

(12)

denote the 1-particle Hamiltonian. Suppose $U_C$ is a sufficiently regular function of $|\hat{R}_\alpha - \vec{r}|$, so that the integral kernel of $\rho^{(1)} = \exp[\beta h^{(1)}]$ admits the Feynman-Kac representation [13, 14], viz.,

$$\rho(\vec{r},\vec{r}') = \int_{\Omega^0} d\mu_{\vec{r},\vec{r}'}(\omega) \exp \left[ -\sum_\alpha \beta \int_0^\beta U_C(\omega(s)) ds \right]$$

(13)

where $U_C(\vec{r}) = U_C(\hat{R}_\alpha - \vec{r})$. Due to randomness of ion positions $\hat{R}_\alpha$, $\rho(\vec{r},\vec{r}')$ is equal to its space average $\langle \rho(\vec{r},\vec{r}') \rangle_\Lambda$ over these positions [15, 16]. In order to evaluate $\langle \rho(\vec{r},\vec{r}') \rangle_\Lambda$, let us note that $U_C(\vec{r})$ is negative-valued and has a finite minimum [17]. Suppose it admits a Taylor expansion in the neighbourhood of this minimum at $\vec{r}_0\alpha$ and that $\beta$ is sufficiently large. Then

$$\langle \rho(\vec{r},\vec{r}') \rangle_\Lambda = |\Lambda|^{-M} \prod_{\alpha = 1}^M \int_\Lambda d^3R_\alpha \rho(\vec{r},\vec{r}')$$

(14)

can be evaluated by expanding $U_C(\hat{R}_\alpha - \vec{r})$ up to second order and applying the method of steepest descent. Evaluation of the average (14) thus amounts to calculating the integral

$$\prod_\alpha \int_\Lambda d^3R_\alpha \exp \left[ -\beta u_0 - \frac{1}{2} u_2 \int_0^\beta \sum_{q=1}^3 (R_{\alpha q} - r_{0\alpha q} - \omega_q(s))^2 ds + \ldots \right]$$

(15)

where $u_0 = U_C(\hat{R}_\alpha - \vec{r}_0\alpha)$, $u_2 = U''_C(\hat{R}_\alpha - \vec{r}_0\alpha)$. This is done in Appendix A.

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One obtains for sufficiently large $\beta$

$$
\left\langle \rho \left( \vec{r}, \vec{r}' \right) \right\rangle \Lambda = Z_1 \int \frac{d\mu_{\vec{r},\vec{r}'}}{\Omega_0} \int \frac{d^3 \vec{r}}{\mathbb{R}^3} \exp \left[ -\beta M u_0 - \frac{1}{2} M u_2 \sum_{q=1}^{3} \int_{0}^{\omega_q(s)} \frac{1}{2} \left( \omega_q(s) - \lambda_q \right)^2 ds \right] d\lambda_1 d\lambda_2 d\lambda_3
$$

where

$$
Z_1 = |\Lambda|^{-M} \left( \frac{2\pi}{\beta u_2} \right)^{\frac{1}{2} (M-1)} M^{3/2}
$$

The integral kernel (16) thus represents, up to a constant factor, the kernel of the canonical density operator of a particle oscillating around a point $\vec{\lambda}$, integrated over all positions $\vec{\lambda} \in \mathbb{R}^3$. In other words,

$$
|\Lambda|^{-M} \prod_{\alpha} \int d^3 R_\alpha \rho \left( \vec{r}, \vec{r}' \right) = Z_1 \int d^3 \lambda \exp \left[ -\beta h^{(1)}_{\text{osc}} (\vec{\lambda}) \right]
$$

where

$$
h^{(1)}_{\text{osc}} (\vec{\lambda}) = -\frac{\hbar^2}{2m} \Delta + \frac{1}{2} M u_2 \left( \vec{r} - \vec{\lambda} \right)^2.
$$

The integral kernel of $\exp \left[ -\beta h^{(1)}_{\text{osc}} (\vec{\lambda}) \right]$ is \[13, 14, 18\]

$$
\rho^{(1)}_{\text{osc}} (\vec{r}, \vec{r}') = \xi^3 \exp \left[ -\frac{1}{2} a \left( \left( \vec{r} - \vec{\lambda} \right)^2 + \left( \vec{r}' - \vec{\lambda} \right)^2 \right) + b \left( \vec{r} - \vec{\lambda} \right) \left( \vec{r}' - \vec{\lambda} \right) \right]
$$

with

$$
\xi = \frac{\alpha \left( \tanh \frac{\Omega}{2} \right)^{1/2}}{2\sqrt{\pi} \sinh \frac{\Omega}{2}} , \quad a = \frac{\alpha^2 \coth \Omega}{\sinh \Omega} , \quad b = \frac{\alpha^2}{\sinh \Omega},
$$

$$
\alpha^2 = \frac{\hbar^2 \alpha^2}{2m} , \quad \Omega = \frac{\hbar^2 \alpha^2}{m} \beta.
$$

The integral over $\mathbb{R}^3$ on the rhs of Eq. (16) is thus a product of three 1-dimensional integrals

$$
\int_{-\infty}^{\infty} d\lambda \exp \left[ -\frac{1}{2} a \left( x - \lambda \right)^2 + b \left( x - \lambda \right) \left( x' - \lambda \right) \right] = \sqrt{\frac{\pi}{a - b}} \exp \left[ -\frac{1}{4} (a + b) (x - x')^2 \right]
$$

each of which is equal to the integral kernel of the operator \[13, 14\]

$$
\sqrt{\frac{\pi}{a - b}} \sqrt{2\pi t_0} \exp \left[ -t_0 T_0 \right] = \frac{2\pi}{\sqrt{a^2 - b^2}} \exp \left[ -t_0 T_0 \right],
$$

(21)
where
\[ t_0 = \frac{2}{a + b} = 2\alpha^{-2} \tanh \frac{1}{2}\Omega, \quad T_0 = -\frac{1}{2} \frac{d^2}{dx^2}. \]

One finds
\[ t_0 T_0 = t(u_2, \beta) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) = t(u_2, \beta) H_{0x}^{(1)} \tag{22} \]
with
\[ t(u_2, \beta) = \delta^{-1} \tanh(\delta\beta), \quad \delta = \frac{\hbar^2}{2m} \alpha^2. \]

Combining Eqs. (16), (20), (21), (22), one obtains for large \( \beta \) the asymptotic equality
\[ \langle \rho(\vec{r}, \vec{r'}) \rangle_{\Lambda} = Z_0(u_0, u_2)(2\pi t_0)^{-3/2} \exp \left[ -\frac{1}{2t_0} \left( \vec{r} - \vec{r'} \right)^2 \right], \tag{23} \]
where
\[ Z_0(u_0, u_2) = |\Lambda|^{-M} \left( \frac{2\pi}{\beta u_2} \right)^{\frac{1}{2}(M-1)} M^{3/2} \xi^3 \left( \frac{2\pi}{\alpha^2} \right)^3 \exp \left[ -\beta Mu_0 \right]. \]

Thus
\[ \langle \rho^{(1)} \rangle_{\Lambda} = Z_0 \exp \left[ -tH_0^{(1)} \right] \tag{24} \]
In the low-temperature régime, \( \langle \rho^{(1)} \rangle_{\Lambda} \) is thus equal, up to a normalization factor, to the canonical density operator of a free particle at an effective temperature \( (k_B t)^{-1} = (k_B\beta)^{-1} = T \).

3 Mean-field impurity heat capacity

Formulae for s-d system’s mean-field energy \( \Delta U_{s-d} \) and heat capacity \( \Delta C \), relative to that of free electrons, will be now derived, using the Hamiltonian \( h^{(n,M)} \), and compared with experimental data on impurity heat capacity of CuCr [10] and LaCeAl$_2$ [12].

3.1 CuCr alloys

According to Monod et al. [19] the spin of the Cr$^{3+}$ ions in CuCr alloys equals 3/2. The impurity expectation energy in these alloys therefore equals
\[ U_{imp} = \left\langle \frac{h^{(M)}}{h^{(M)}} \right\rangle_{\Lambda} \]
\[ = -M n^2 f_2(\xi) + \frac{1}{2} Mg^2 + 4Mg^2 \frac{e^{-\beta g^2}}{e^{-\beta g^2} \cosh (3\beta g\xi \sqrt{n})} \cos (3\beta g\xi \sqrt{n} + \cosh (\beta g\xi \sqrt{n})) \tag{25} \]
$f_1$, defined by Eq. \(7\) is a linear function in the simplest approximation \(45\):

$$f_1(\xi) = b_0 + b_1 \xi$$  (Appendix \[B\]). Then according to Eqs. \(22\), \(44\), the interaction energy of electrons with the Hamiltonian $\tilde{\mathcal{H}}^{(n,M)}(\xi, \eta)$ equals

$$\Delta U_e = \left\langle \tilde{\mathcal{H}}^{(n,M)}(\xi, \eta) \right\rangle - \left\langle A^{(n)} H_0^{(n)} \right\rangle / A^{(n)} H_0^{(n)}$$  (26)

$$= - Mnf_2(\xi) (b_0 + b_1 f_2(\xi) + \ldots).$$

From Eqs. \(8, 25, 26\) one obtains the following expression for $\Delta U_{s-d}$ of a system of $n$ electrons and $M$ impurities with spin $3/2$:

$$\Delta U_{s-d} = U_{\text{imp}} - Mnf_2(\xi) (b_0 + b_1 f_2(\xi) + \ldots) + Mnf_2(\xi) - \frac{1}{2} Mn^2 f_2(\xi)$$  (27)

where $\xi$ is the minimizing solution of Eq. \(6\) with $f_1$ given by Eq. 145.

The number of conduction electrons per host atom in CuCr equals one, and hence the number of these electrons per impurity $n_1 = c^{-1}$.

The $n$-electron, $M$-impurity $s$-$d$ system will be now treated as a subsystem of a sample $S$ containing one mole of impurities. Then $n = Mn_1$. In terms of $n_1$, \(\gamma = \sqrt{M}g\), the energy $\Delta U_m = 6.022 \cdot 10^{23} M^{-1} \Delta U_{s-d}$ of such sample with spin $3/2$ impurities, divided by $c$ and expressed in joules, equals

$$c^{-1} \Delta U_m = \left( \frac{1}{2} \gamma^2 + 4 \gamma^2 \frac{e^{-4\beta\gamma^2 M^{-1}} \cosh (3\beta\gamma \sqrt{m_1})}{e^{-4\beta\gamma^2 M^{-1}} \cosh (3\beta\gamma \sqrt{m_1}) + \cosh (\beta\gamma \sqrt{m_1})} \right) 602.2 \cdot 160.2 M^{-1} n_1$$  (28)

with

$$f_2(\xi) = \frac{\gamma}{M \sqrt{m_1}} \frac{3e^{-4\beta\gamma^2 M^{-1}} \sinh (3\beta\gamma \sqrt{m_1}) + \sinh (\beta\gamma \sqrt{m_1})}{e^{-4\beta\gamma^2 M^{-1}} \cosh (3\beta\gamma \sqrt{m_1}) + \cosh (\beta\gamma \sqrt{m_1})}$$

if $\gamma, b_0$ are given in $\sqrt{eV}$.

Eq. \(6\) takes the form

$$f_3(\xi) = \xi$$  (29)

with $f_3 = b_0 + (b_1 + 1) f_2$.

The excess heat capacity of $S$, relative to that of pure Cu, equals

$$\Delta C(T) = \frac{\partial \Delta U_m}{\partial T} + \frac{\partial \Delta U_m}{\partial \xi} \frac{\partial \xi}{\partial T},$$  (30)

where

$$\frac{\partial \xi}{\partial T} = - \frac{\partial f_3}{\partial T} \left( \frac{\partial f_3}{\partial \xi} - 1 \right)^{-1}.$$  (31)

$\Delta C(T)$ depends on the solution $\xi$ of Eq. \(29\) and on the parameters $b_0, b_1, \gamma, M$. An additional parameter $\Delta T > 0$, equal to the shift of the temperature variable of $\Delta C$, proves necessary. The origins of this shift are explained in Section 2.
Table 1:

| Alloy        | $x$ | $c$      | $n_1$ | $b_0$ $[\sqrt{eV}]$ | $b_1$ | $\gamma$ $[\sqrt{eV}]$ | $M$    | $\Delta T$ [K] |
|--------------|-----|----------|-------|----------------------|-------|-------------------------|--------|----------------|
| CuCr         |     | $\frac{51}{66}$ | $\frac{10^7}{24}$ | $-461$ | $1.09 \cdot 10^{-3}$ | 0.091  | 248500 | 1.05           |
| CuCr         |     | $\frac{212}{66}$ | $\frac{10^7}{24}$ | $-631$ | $1.01 \cdot 10^{-3}$ | 0.086  | $36 \cdot 10^4$ | 0.78           |
| (LaCe) Al$_2$ | $\frac{n_1}{1871}$ | $\frac{2142}{24}$ | $-13101$ | $\frac{12}{66}$ | $\frac{21}{66}$ | 58     | 0.39           |

The best fitting graphs of $c^{-1} \Delta C(T + \Delta T)$ vary with $M$. Moreover, the graphs obtained for $M \gg 1$ provide much better agreement with experiment than those for $M = 1, 2$. The graphs of $c^{-1} \Delta C(T + \Delta T)$ for CuCr with $c = 51$ ppm ($M = 24850$) and $c = 21.2$ ppm ($M = 360000$), plotted in the same units as in Ref. [10], are depicted in Figs. 1, 2. The corresponding values of the remaining parameters $b_0, b_1, \gamma, \Delta T$ are given in Table 1.

The solution $\xi(T)$ of Eq. (29) is unique in both cases and minimizes $f(h^{(n,M)}, \beta)$. The graphs of $\xi(T)$ are plotted in Fig. 3.

It appears that higher order terms of the expansions (42), (45) should be included in order to improve the quality of mean-field $\Delta C/c$.

It is worth noting that since the best fitting values $M_f$ of $M$ are much smaller than $A = 6.022 \cdot 10^{23}$, the sample $S$ can be viewed as consisting of magnetic domains, each containing $M_f$ impurities with a definite favoured impurity-spin orientation, which differs, in general, from one domain to another. Existence of such domains in some magnetic materials has been established experimentally (e.g. Ref. [20]).

3.2 (La$_{1-x}$Ce$_x$) Al$_2$

Experimental data on $\Delta C/c$ of (La$_{1-x}$Ce$_x$) Al$_2$ alloys are presented in Ref. [12]. According to Refs. [12] [21], a typical Kondo effect, without any superconducting side-effects, is observed in (La$_{1-x}$Ce$_x$) Al$_2$ samples with Ce content above $x = 0.0067$. However, according to Bader et al. [12], for $x = 0.0064$ the expected normal-state and measured superconducting-state heat capacities do not differ significantly. Thus a mean-field normal-state theory of $\Delta C/c$ for (La$_{1-x}$Ce$_x$) Al$_2$ with $x = 0.0064$ can be reliable.

The number of valence electrons per host atom in LaAl$_2$ equals $8/3$. For a $x = 0.0064$,

$$c = \frac{0.0064}{2.9936} = \frac{4}{1871}, \quad n_1 = \frac{8}{3} c^{-1} = \frac{3742}{3}.$$  

Since the spin of Ce ions equals $1/2$ [12], therefore

$$f_2(\xi) = \frac{\gamma}{M \sqrt{n_1}} \tanh (\beta \gamma \xi \sqrt{n_1})$$  (32)
The mean-field impurity heat capacity of CuCr with $c = 51$ ppm and values of $b_0, b_1, \gamma, M, \Delta T$ given in Table 1. The points are experimental results from Ref. [10].
Figure 2: The mean-field impurity heat capacity of CuCr with $c = 21.2$ ppm and values of $b_0$, $b_1$, $\gamma$, $M$, $\Delta T$ given in Table 1. The points are experimental results from Ref. [10].
Figure 3: The solution ξ(T) of Eq. (29) for CuCr with values of \( \theta_0, b_1, \gamma, M, \Delta T \) given in Table I.
Figure 4: The mean-field impurity heat capacity of $(\text{La}_{1-x}\text{Ce}_x)\text{Al}_2$ with $x = 0.0064$ and values of $b_0, b_1, \gamma, M, \Delta T$ given in Table 1. The points are experimental results from Ref. [12].

and $\Delta U_m/c$ for a sample $S$ of $(\text{La}_{1-x}\text{Ce}_x)\text{Al}_2$, expressed in joules, equals

$$e^{-1}\Delta U_m = \left( \frac{1}{2} \gamma^2 - \frac{1}{2} M^2 n_1 f_2^2(\xi) - M^2 n_1 f_2(\xi) [b_0 + b_1 f_2(\xi) + \ldots] \right) \frac{1}{4} \cdot 602.2 \cdot 160.2 \cdot 1871 M^{-1}$$

(33)

if Eq. (44) is used and $b_0, \gamma, \beta, \xi$ are given in powers of eV.

The mean-field $\Delta C/c$ curve best fitting to experimental $\Delta C/c$ of Ref. [12] was obtained for $M = 40$ and is depicted in Fig. 4. The corresponding values of other parameters are given in Table 1. Since the error of experimental $\Delta C/c$ values is relatively high above 5 K [12], the mean-field $\Delta C/c$ curve in Fig. 4 provides a good fit to experiment.

The equation $f_3(\xi) = \xi$ for $\xi(T)$ has a unique minimising solution with $\xi(T) \in (11 \cdot 10^{-5} \sqrt{\text{eV}}, 19 \cdot 10^{-5} \sqrt{\text{eV}})$ for $T \in (0.015 \text{ K}, 10 \text{ K})$. The graph of $\xi(T)$ is, similar as those for CuCr in Fig. 3, increasing in $T$. 

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4 Concluding remarks

Progress has been made in improving the quality of theoretical impurity heat capacity graphs $\Delta C(T)$ of DMA. Scaling procedures, used in previous s-d theories to adjust thermodynamic functions to experimental data, were unnecessary and nonlinear dependence of $\Delta C(T)$ on impurity concentration $c$ in CuCr has been accounted for the first time.

The mean-field theory of a dilute s-d system established in Ref. [11] has also proved capable of explaining the temperature dependence of impurity heat capacity $\Delta C$ of $(La_{1-x}Ce_x)Al_2$ with $x = 0.0064$. Partial quantitative agreement between theory and experiment has been achieved for CuCr alloys, especially for the smaller value of impurity concentration considered.

Higher order terms of the expansion of $f_1$ should be included in order to improve these results.

A

The integral (15) is an $M$-fold product of 3-dimensional integrals

$$ I = \int_{\Lambda} d^3R \exp \left[ -\frac{1}{2} u_2 \int_0^\beta \sum_{q=1}^3 (R_q - r_{0q} - \omega_q(s))^2 \, ds \right] $$

and $\exp \left[ -\beta M u_0 \right]$. The representation (16) of $\left< \rho(\vec{r}, \vec{r}') \right>_{\Lambda}$, for large $\beta$, obtains by applying to the $I$ the dominated convergence theorem (in order to express the integral in the exponent as a limit of partial sums) and the method of steepest descent:

$$ I = \lim_{m \to \infty} \int_{\Lambda} d^3R \exp \left[ -\frac{\beta}{2m} u_2 \sum_{k=1}^m \sum_{q} (R_q - r_{0q} - x_{kq})^2 \right] $$

$$ \approx \lim_{m \to \infty} \int_{R^3} d^3R \exp \left[ -\frac{\beta}{2m} u_2 \sum_{kq} x_{kq}^2 \right. $$

$$ -\frac{\beta}{2m} u_2 \sum_{q} \left( \frac{1}{\sqrt{m}} \sum_{k} x_{kq} - \sqrt{m} (R_q - r_{0q}) \right)^2 + \frac{\beta}{2m^2} u_2 \sum_{q} \left( \sum_{k} x_{kq} \right)^2 \right] $$

$$ = \lim_{m \to \infty} \left( \frac{2\pi}{\beta u_2} \right)^{3/2} \exp \left[ -\frac{\beta}{2m} u_2 \sum_{kq} x_{kq}^2 + \frac{\beta}{2m^2} u_2 \sum_{q} \left( \sum_{k} x_{kq} \right)^2 \right] $$

$$ = \left( \frac{2\pi}{\beta u_2} \right)^{3/2} \exp \left[ -\frac{1}{2} u_2 \beta \int_0^\beta \omega^2(s) \, ds + \frac{1}{2} \beta^{-1} u_2 \sum_{q} \left( \int_0^\beta w_q(s) \, ds \right)^2 \right], \quad (35) \]
where \( x_kq = \omega_q \left( \frac{kq}{m} \right) \). The squared integral in the exponent can be linearized, using the identity

\[
\exp(a^2) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} \exp \left[ -\frac{1}{2} \xi^2 + \sqrt{2}a\xi \right] d\xi
\]

which yields

\[
I^M = \left( \frac{2\pi}{\beta u_2} \right)^{3M/2} \exp \left[ -\frac{1}{2} Mu_2 \omega^2(s) ds + \frac{1}{2} \beta^{-1} Mu_2 \sum_q \left( \int_0^\beta w_q(s) ds \right)^2 \right] \]

\[
= (2\pi)^{-3/2} \left( \frac{2\pi}{\beta u_2} \right)^{3M/2} \int_{\mathbb{R}^3} d\xi_1 d\xi_2 d\xi_3 \exp \left[ -\frac{1}{2} \sum_s \xi_s^2 \right. \\
\left. - \frac{1}{2} Mu_2 \int_0^\beta \omega^2(s) ds + \sqrt{\beta^{-1} Mu_2} \sum_q \xi_q \int_0^\beta \omega_q(s) ds \right] \]

\[
= \left( \frac{2\pi}{\beta u_2} \right)^{3(M-1)/2} M^{3/2} \int_{\mathbb{R}^3} d\lambda_1 d\lambda_2 d\lambda_3 \exp \left[ -\frac{1}{2} Mu_2 \sum_q \int_0^\beta (\omega_q(s) - \lambda_q)^2 ds \right]
\]

in accord with Eq. (16).

\[ \text{B} \]

The form of \( f_1 \) defined by Eq. (7) is crucial in the mean-field theory of the s-d system. Here \( f_1 \) is derived under the assumption that \( \tilde{h}_{e_1}^{(1, M)}(\xi, \eta) \) is defined in terms of a function \( -g \sqrt{n} U \left( \vec{R}_e - \vec{r} \right) \), which has absolute maximum equal \( v_0 \) and absolute minimum equal \( u_0 \), and that the expansion in (15) is terminated on the first term. The space average of \( \exp \left[ -\beta \tilde{h}_{e_1}^{(1, M)}(\xi, 0) \right] \) over impurity positions then equals

\[
\langle \exp \left[ -\beta \tilde{h}_{e_1}^{(1, M)}(\xi, 0) \right] \rangle_A = \begin{cases} 
\exp \left[ -\beta H_0^{(1)} - \beta Mu_0 \xi \right] & \text{for } \sigma_z = 1 \\
\exp \left[ -\beta H_0^{(1)} + \beta Mu_0 \xi \right] & \text{for } \sigma_z = -1 
\end{cases}
\]

and Eq. (10) for \( z \) takes the form

\[
\frac{4\pi v}{\hbar^3} \int_0^\infty dp \ p^2 \left\{ \left( z^{-1} \exp \left[ \beta \left( Mu_0 \xi + \frac{p^2}{2m} \right) \right] + 1 \right)^{-1} \right. \\
\left. + \left( z^{-1} \exp \left[ \beta \left( -Mu_0 \xi + \frac{p^2}{2m} \right) \right] + 1 \right)^{-1} \right\} = 1.
\]
where \( v = |\Lambda|\mu^{-1} \). Following Huang [22], one transforms Eq. (37) to
\[
v\lambda_0^{-3} \left( f_{3/2} \left( ze^{-\beta M_u \xi} \right) + f_{3/2} \left( ze^{\beta M_v \xi} \right) \right) = 1, \tag{38}
\]
where
\[
v\lambda_0^{-3} = \frac{1}{8} 3\sqrt{\pi} (\beta\varepsilon_F)^{-3/2}.
\]
For large \( z \), \( f_{3/2}(z) \) is given by Sommerfeld’s expansion:
\[
f_{3/2}(z) = \frac{4}{3\sqrt{\pi}} \left( (\ln z)^{3/2} + \frac{\pi^2}{8} (\ln z)^{-1/2} + \ldots \right). \tag{39}
\]
Let \( Mu_0\xi^{1-1} = \mu \), \( Mv_0\xi^{1-1} = \nu \). Then \( z \) satisfying Eq. (38) is given by the expansion
\[
\ln z = a_1\beta\varepsilon_F + a_0 + a_{-1} (\beta\varepsilon_F)^{-1} + \ldots \tag{40}
\]
with
\[
a_1(\xi) = 1 + \frac{1}{2} (\mu - \nu) - \frac{1}{16} (\mu + \nu)^2 + \ldots
\]
\[
a_0 = 0
\]
\[
a_{-1}(\xi) = \frac{\pi^2}{12} \left( 1 - \frac{1}{4} (\mu + \nu)^2 \right)^{-1/2} = -\frac{\pi^2}{12} \left( 1 + \frac{1}{8} (\mu + \nu)^2 + \ldots \right),
\]
From Eq. (7) one finds (cf. Ref. [11])
\[
f_1(\xi) = (Mn\beta)^{-1} \frac{\partial}{\partial \xi} \text{Tr} \ln \left( 1 + z\rho^{(1)} \right).
\]
Hence
\[
f_1(\xi) = v\lambda_0^{-3} \left( -u_0 f_{3/2} \left( ze^{-\beta M_u \xi} \right) + v_0 f_{3/2} \left( ze^{\beta M_v \xi} \right) \right)
= b_0 + b_1\xi - \frac{\pi^2}{8} b_0 (\beta\varepsilon_F)^{-2} + \ldots \tag{41}
\]
with
\[
b_0 = \frac{1}{2} (v_0 - u_0) , \quad b_1 = \frac{3M}{8\varepsilon_F} (u_0 + v_0)^2.
\]
The energy of the electrons’ subsystem also expresses in terms of \( f_1 \). According to Eqs. (38), (7)
\[
\left< n\Gamma_1^n h_{e^1(1,M)}^{(1)}(\xi,\eta) \right>_{n\Gamma_1^n h_{e}^{1(M)}(\xi,\eta)}
= \left< n\Gamma_1^n H_0^{(1)} \right>_{n\Gamma_1^n h_{e}^{1(M)}(\xi,\eta)} - nM f_2(\xi) (b_0 + b_1 f_2(\xi) + \ldots) \tag{42}
\]
The first term on the rhs of Eq. (42) can be evaluated in a similar manner as the energy of a free Fermi gas, viz.,

\[
\left\langle n\Gamma_{f}^{0} H_{0}^{(1)} \right\rangle_{n\Gamma_{f}^{0} \tilde{h}_{e}^{(1),M}(\xi, \eta)} = \frac{3n}{10} \varepsilon_{f}^{-3/2} \beta^{-5/2} \left\{ \left( \ln z - \beta M u_{0} (\xi - \eta) \right)^{5/2} + \frac{5}{8} \pi^{2} \left( \ln z - \beta M u_{0} (\xi - \eta) \right)^{1/2} + \ldots \right\} \\
+ \left( \ln z + \beta M v_{0} (\xi - \eta) \right)^{5/2} + \frac{5}{8} \pi^{2} \left( \ln z + \beta M v_{0} (\xi - \eta) \right)^{1/2} + \ldots \right\} \\
= \frac{3n}{10} \varepsilon_{f}^{-3/2} \left\{ 2 + 5a_{-1} (\xi - \eta) (\beta \varepsilon_{F})^{-2} + \frac{5}{4} \pi^{2} (\beta \varepsilon_{F})^{-2} + \frac{5}{8} M^{2} (u_{0} + v_{0})^{2} \varepsilon_{F}^{-2} (\xi - \eta)^{2} + \ldots \right\} \\
= \left\langle n\Gamma_{f}^{0} H_{0}^{(1)} \right\rangle_{n\Gamma_{f}^{0} H_{0}^{(1)}} - \frac{\pi^{2}}{24} nM b_{1} (\xi - \eta)^{2} (\beta \varepsilon_{F})^{-2} + \frac{1}{2} nM b_{1} (\xi - \eta)^{2} + \ldots \right\} \\
(43)
\]

If the Taylor expansions of \( U_{\alpha}(\vec{r}) \) around the absolute maximum and absolute minimum are cut off on the second derivatives, the structure of \( f_{1} \), as well as that of the expectation values (42), (43), changes, e.g. under the approximations of Section 2. \( f_{1} \) is no longer regular at \( \xi = 0 \):

\[
f_{1}(\xi) = v \left\{ \lambda_{0} (t (u_{2}, \beta))^{-3} \frac{\partial Z_{0} (u_{0} \xi, u_{2} \xi)}{\partial \xi} f_{3/2} (z Z_{0} (u_{0} \xi, u_{2} \xi)) + \lambda_{0} (t (-v_{2}, \beta))^{-3} \frac{\partial Z_{0} (-v_{0} \xi, -v_{2} \xi)}{\partial \xi} f_{3/2} (z Z_{0} (-v_{0} \xi, -v_{2} \xi)) \right\},
\]

with

\[
v \lambda_{0}^{-3}(t) = \frac{1}{8} 3 \sqrt{\pi} (t \varepsilon_{F})^{-3/2}
\]

\((u_{2} (v_{2})\) denoting the second derivative of \(-g \sqrt{nU} (\vec{R}_{\alpha} - \vec{r})\) at the absolute minimum (maximum) and the corresponding coefficient \( b_{1}' \), in the new expansion of \( f_{1} \) around \( \xi_{0} \neq 0 \), will differ from \( b_{1}' \) resulting in the modified Eq. (43).

In view of the presumable smallness of

\[
\Delta U_{0} = \left\langle n\Gamma_{f}^{0} H_{0}^{(1)} \right\rangle_{n\Gamma_{f}^{0} \tilde{h}_{e}^{(1),M}(\xi, \eta)} - \left\langle n\Gamma_{f}^{0} H_{0}^{(1)} \right\rangle_{n\Gamma_{f}^{0} H_{0}^{(1)}}
\]

where \( \tilde{h}_{e}^{(1),M} = n\Gamma_{f}^{0} \tilde{h}_{e}^{(1),M} \), these modifications can be exploited in the simplest manner by restricting \( u_{0}, \ v_{0}, \ u_{2}, \ v_{2} \) to values for which \( b_{1}' \) vanishes. As a consequence,

\[
\Delta U_{0} \approx 0 \quad (44)
\]

whereas the range of \( b_{1}' \) can be expected to include also negative values. Thus, in general,

\[
f_{1}(\xi) = b_{0}' + b_{1}' \xi + \ldots \quad , \quad b_{0}', b_{1}' \in \mathbb{R}^{1}
\]
References

[1] J. Kondo. Prog. Theor. Phys., 32:37, 1964.
[2] P. E. Bloomfield and D. R. Hamann. Phys. Rev., 164:856, 1967.
[3] K. G. Wilson. Rev. Mod. Phys., 47:773, 1975.
[4] V. T. Rajan, J. H. Lowenstein, and N. Andrei. Phys. Rev. Lett., 49:497, 1982.
[5] N. Andrei, K. Furuya, and J. H. Lowenstein. Rev. Mod. Phys., 55:331, 1983.
[6] V. M. Filyov, A. M. Tsvelik, and P. B. Wiegmann. Phys. Lett. A, 81:115, 1981.
[7] P. B. Wiegmann. An exact solution of the Kondo problem. In I. M. Lifshits, editor, Quantum Theory of Solids. MIR Publishers, Moscow, 1982.
[8] A. C. Hewson. The Kondo Problem to Heavy Fermions. Cambridge University Press, Cambridge, 1993.
[9] J. Maćkowiak. Phys. Rep., 308:235, 1999.
[10] B. B. Triplett and N. E. Philips. Phys. Rev. Lett., 27:1001, 1971.
[11] J. Maćkowiak. Physica A, 336:461, 2004.
[12] S. D. Bader, N. E. Philips, M. B. Maple, and C. A. Luengo. Solid State Commun., 16:1263, 1975.
[13] B. Simon. Functional Integration and Quantum Physics. Academic Press, New York, San Francisco, London, 1979.
[14] J. Glimm and A. Jaffe. Quantum Physics, A Functional Integral Point of View. Springer, New York, Heidelberg, Berlin, 1981.
[15] S. F. Edwards. Phil. Mag., 3:1020, 1958.
[16] V. Ambegaokar. The Green’s Function Method. In R. D. Parks, editor, Superconductivity. Marcel Dekker, Inc., New York, 1969.
[17] J. M. Ziman. Principles of the Theory of Solids. Cambridge University Press, Cambridge, 1972.
[18] S. Pruski and J. Maćkowiak. Rep. Math. Phys., 1:309, 1971.
[19] P. Monod and S. Schultz. Phys. Rev., 173:645, 1968.
[20] A. Aharoni. Introduction to the Theory of Ferromagnetism. Oxford University Press, 2000.
[21] W. Felsch, K. Winzer, and G. V. Minnigerode. Z. Physik B, 21:151, 1975.
[22] K. Huang. Statistical Mechanics. Wiley Inc., New York, London, 1963.