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PERTURBATION THEORY FOR THE IMPURITY SPECIFIC HEAT OF DILUTE MAGNETIC ALLOYS*

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Second order perturbation theory for the free energy of the s–d exchange Hamiltonian $H_{\rm K}$ is applied to CuCr. The temperature dependence of the cutoff $D(T)$ for $H_{\rm K}$ is adjusted to obtain agreement between theory and the experimental plot of specific heat for CuCr found by Tripplett and Philips. We find that the function $D(T)$ follows approximately the rule $D(T) = 10^3 k_{\rm B}T + \gamma(k_{\rm B}T)^2$.

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1. Introduction

The theory of Dilute Magnetic Alloys (DMA) initiated by Kondo in 1964 [1] has only partially succeeded in explaining the intriguing properties of these materials. Kondo's theory and its extension [2–4] explain the presence of an anomalous resistivity minimum in the range of low temperatures. It is founded on the concept of s–d exchange interaction [5] between the spin density of conduction electrons and M impurity atoms endowed with magnetic moments $\frac{1}{2}\boldsymbol{S}$:

$$V_{\rm K}(M) = -\frac{1}{2}J\sum_{\alpha=1}^{M}\sum_{u=x,y,z}\sigma_u(\boldsymbol{R}_\alpha)S_{u\alpha}, \qquad J<0\,, \tag{1}$$

where σ_u denotes the electron spin density.

Since the early seventies, the single impurity version of the Kasuya Hamiltonian

$$H_{\rm K}(1) = \sum_{\boldsymbol{k}\sigma}\varepsilon_k a^*_{\boldsymbol{k}\sigma}a_{\boldsymbol{k}\sigma} + V_{\rm K}(1) = H_0 + V_{\rm K}(1) \tag{2}$$

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attracted the attention of theorists. Wilson and others [6–8] applied the Renormalization Group Technique (RGT) to the VG Hamiltonian which maps onto $H_{\mathrm{K}}(1)$ and showed that the specific heat of $H_{\mathrm{K}}(1)$ exhibits a peak in the vicinity of the Kondo temperature T_{K}. Such a peak is observed in the high temperature, magnetically disordered phase of several DMA (*e.g.* Refs. [9–11]).

Andrei [12] and Wiegmann [13] independently diagonalized the Hamiltonian $H_{\mathrm{K}}(1)$. The resulting thermodynamics of $H_{\mathrm{K}}(1)$ was studied by Andrei *et al.* [14] in the scaling regime: B, $k_{\mathrm{B}}T \ll D$ with $T_0 = D\exp(-\Pi/c_0)$ fixed as $c_0 = 2J/(1-3/4J^2) \to 0$, $D \to \infty$ (B denoting the magnetic field and D the cutoff imposed on V_{K}). They obtained a peak in the graph of impurity specific heat which coincides with the one found by Oliveira *et al.* [8]. Other thermodynamic functions were also examined. Unfortunately, direct comparison of these graphs with experiment is impossible due to the absence of a fundamental parameter in single-impurity theories of DMA — the impurity concentration $c = MN^{-1}$. There is convincing experimental evidence that all properties of DMA, in particular impurity specific heat, are affected by variations of c (*e.g.* Refs. [1, 9–11, 15, 16]).

Our objective is to establish a theory of DMA founded on the M impurity Hamiltonian $H_{\mathrm{K}}(M)$, which incorporates the theory of resistivity of DMA due to Kondo and accounts for the dependence of all DMA properties on c. A preliminary step in this direction was made in Ref. [18], where 2nd order perturbation theory for the free energy $f(H_{\mathrm{K}}(M),T)$ per conduction electron of $H_{\mathrm{K}}(M)$ was developed. In the magnetically disordered phase of DMA the appropriate unperturbed Hamiltonian is that of the free electron gas H_0. The difference $f(H_{\mathrm{K}}(M),T) - f(H_0,T) = f_2(T)$ up to 2nd order in V_{K} equals:

$$f_2(T) = \frac{3J^2c}{4Nn} z_{\mathrm{F}} \sum_{\boldsymbol{k},\boldsymbol{k}'} (1-f_{\mathrm{F}}(\varepsilon_k))(1-f_{\mathrm{F}}(\varepsilon_{k'})) \frac{\mathrm{e}^{-\beta\varepsilon_k} - \mathrm{e}^{-\beta\varepsilon_{k'}}}{\varepsilon_k - \varepsilon_{k'}} \,. \tag{3}$$

The expression (3) is obtained for spin 1/2 impurities. Larger values of impurity spin introduce an additional constant factor. n stands for the number of conduction electrons, N represents the number of atoms of the host metal, ε_{F} denotes the Fermi level, $z_{\mathrm{F}} = \exp(\beta\varepsilon_{\mathrm{F}})$ and $f_{\mathrm{F}}(\varepsilon) = (1 + z_{\mathrm{F}}^{-1}\exp(\beta\varepsilon))^{-1}$.

Passing from the summation over momenta to integration over $\varepsilon_k = \hbar^2k^2/2m$ one obtains

$$c^{-1}f_2(T) = \frac{3J^2m^3|\Lambda|^2}{4Nn\pi^4\hbar^6} \int\limits_{\varepsilon_{\mathrm{F}}-D}^{\varepsilon_{\mathrm{F}}+D} d\varepsilon \int\limits_{\varepsilon_{\mathrm{F}}-D}^{\varepsilon_{\mathrm{F}}+D} d\varepsilon' f_{\mathrm{F}}(\varepsilon)\left(1 - f_{\mathrm{F}}\left(\varepsilon'\right)\right) \frac{\sqrt{\varepsilon\varepsilon'}}{\varepsilon - \varepsilon'} \,, \tag{4}$$

where m denotes the electron mass and, similarly as in Refs. [12,13], a cutoff D on the range of interaction V_{K} has been imposed. In other words, we assume that only those valence electrons which have energies within a thin band around the Fermi level: $\varepsilon \in [\varepsilon_{\mathrm{F}} - D, \varepsilon_{\mathrm{F}} + D]$, are capable of conveying the s–d exchange. Furthermore, we assume that D is temperature dependent and adjust $D(T)$ to fit the theoretical impurity free energy $c^{-1}Nf_2(T)$ to the experimental curve $\Delta\, c_i\, e(T)/c$ found by Tripplett and Philips for CuCr with Cr concentration $c = 51 \times 10^{-6}$ [9]. The adjusted function $D(T)$ has the form

$$D(T) = 10^3 k_{\mathrm{B}}T + a(T)\,, \tag{5}$$

where $a(T)$ is a positive valued increasing, convex function of the order of $10^{-4}D(T)$, approximately expressed by the formula $a(T) = \gamma(k_{\mathrm{B}}T)^2$, $\gamma = 2.10273 \times 10^3 (\mathrm{eV})^{-1}$. A constant D fails to yield agreement with experiment. Details of the calculations and resulting plot of $D(T)$ are given in the next section.

2. The impurity specific heat curve of CuCr

A well known example of a peak in the impurity specific heat of DMA is the one found by Tripplett and Philips [9] for CuCr with c ranging between 21.2×10^{-6} and 51×10^{-6}. Rapid increase of $c^{-1}\Delta c_{ie}(T)$ for CuCr with $c = 51 \times 10^{-6}$ below $T_c = 0.07$ K (*cf.* Fig. 1 of Ref. [9]) indicates the presence of a 2nd order phase transition at T_c. The range of temperatures $T > T_c$ for $c < 51 \times 10^{-6}$ thus corresponds to the magnetically disordered phase, where the appropriate unperturbed Hamiltonian for H_{K} is H_0 and where Eqs. (3), (4) can be applied.

The expression (4) allows an exact fit of the resulting theoretical curve of $c^{-1}\Delta c_i(T)$ to the experimental one by adjusting the cutoff function $D(T)$. We have verified that $D(T)$ of the form given by Eq. (5) yields a good fit of $c^{-1}\Delta c_i(T)$ to the experimental curve plotted in Fig. 1 of Ref. [9]. The graph of the nonlinear part of $D(T)$ viz. $D(T)$ — $10^3 k_{\mathrm{B}}T$, is plotted in Fig. 1

The resulting plot of $c^{-1}Nf_2(T)$ is concave and decreasing in T, in accord with the inequalities

$$-T\frac{\partial^2 f}{\partial T^2} > 0, \qquad s = -\frac{\partial f}{\partial T} \geq 0\,, \tag{6}$$

satisfied by the free energy f and entropy s.

A constant D fails to yield agreement with experiment, presumably due to the large width of the temperature window encountered. The resulting theory is therefore no longer a microscopic one, as it requires introduction of a temperature dependent support for $V_{\mathrm{K}}(M)$. The d electrons in the iron transition series metals are known to be largely conduction electrons [19].

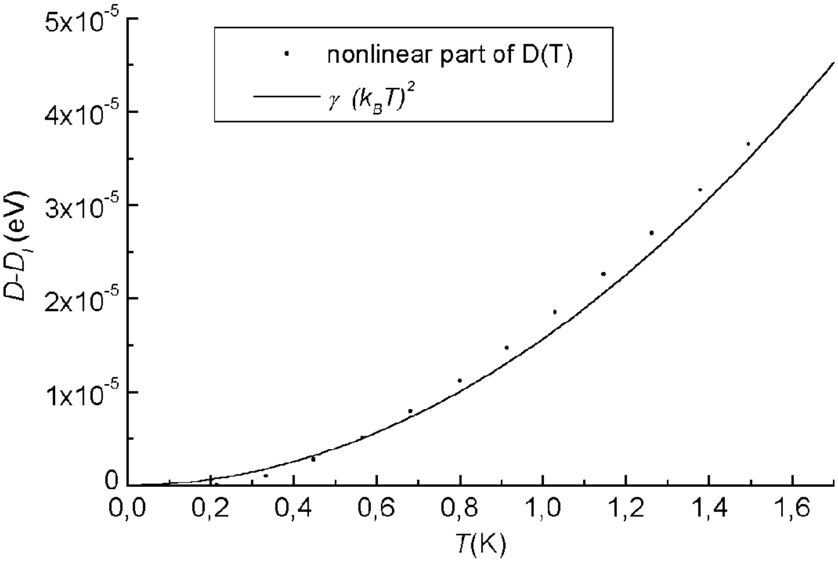

Fig. 1. Nonlinear part of the cutoff $D(T)$ and its quadratic approximation adjusted to give the agreement between theory and the experimental data depicted in Fig. 1 of Ref. [9].

It is therefore difficult to estimate the real values of magnetic moments of atoms belonging to this series. However, since the magnitude of this moment for impurities in DMA introduces only a constant factor into the r.h.s. of Eqs. (3), (4), we assume for simplicity that below 10 K only the s electron of Cr contributes to the gas of conduction electrons in CuCr and that the spin of the resulting Cr^+ ions equals 1/2. Under this assumption, $S = 1$ in Eq. (1) for CuCr and Eqs. (3), (4) remain valid.

The quantity plotted in Fig. 1 of Ref. [9] is

$$c^{-1}\Delta c_{ie} = -Nc^{-1}T\frac{\partial^2}{\partial T^2}(f_{\mathrm{CuCr}} - f_{\mathrm{Cu}}) \tag{7}$$

in J/(K mole Cr) units, where f_{CuCr} denotes the free energy per conducting electron for CuCr and f_{Cu} that for the electron gas of pure Cu. One mole of Cr is contained in $c^{-1} = 10^6/51$ moles of CuCr, therefore

$$\begin{aligned} N &= c^{-1}(1-c)\,6.022 \times 10^{23}\,, \\ n &= c^{-1}\,6.022 \times 10^{23}\,. \end{aligned}$$

The system volume $|\Lambda|$ is equal, up to sufficient approximation, to that of $c^{-1}(1-c)$ moles of Cu, that is, 1246470.588 g of Cu at about 5 K. Thus

$$|\Lambda| = |\Lambda_{20}|(1-\alpha\Delta)^3 = 137600.5586\mathrm{cm}^3,$$

$|\Lambda_{20}|$ denoting the volume at 20°C, $\alpha = 16.5\times 10^{-6}\mathrm{K}^{-1}$. For the Fermi level ε_{F} in Eqs. (3), (4) we substitute the Fermi level of Cu: $\varepsilon_{\mathrm{F}} = 7.1$ eV. Approximating the derivative on the r.h.s. of Eq. (7) by $-T_2(\Delta T)^{-2}(\Delta_2 f_2 - \Delta_1 f_2)$, where

$$\Delta_2 f_2 = f_2(T_3) - f_2(T_2)\,, \qquad \Delta_1 f_2 = f_2(T_2) - f_2(T_1)\,,$$

and $k_{\mathrm{B}}\Delta T = k_{\mathrm{B}}(T_3 - T_2) = k_{\mathrm{B}}(T_2 - T_1) = 10^{-5}$ eV, one obtains agreement between $c^{-1}\Delta c_{ie}$ and $c^{-1}\Delta c_i$ at $T_2 = 0.216$ K for $J = -0.0028943$ eV and $D(0.1\mathrm{K}) = 0.0086\mathrm{eV} = 10^2 k_{\mathrm{B}}\mathrm{K}$. The fit of $c^{-1}\Delta c_i$ to $c^{-1}\Delta c_{ie}$ at $T > 0.216$ K results by adjusting $D(T)$ according to Eq. (5) for the fixed value of J.

The integral I on the r.h.s. of Eq. (4) was evaluated numerically for successive values of T and $D(T)$.

For I one obtains the following expression

$$\begin{aligned} I &= g_0(D,q) + g_1(D,q) + g_2(D,q) \\ &\quad + 2\int_{\varepsilon_{\mathrm{F}}-D}^{\varepsilon_{\mathrm{F}}+D} d\varepsilon f_{\mathrm{F}}(\varepsilon)\sqrt{\varepsilon}\left[\sqrt{\varepsilon_{\mathrm{F}}-D} - \sqrt{\varepsilon_{\mathrm{F}}+D}\,\right] \\ &\quad + 2\int_{\varepsilon_{\mathrm{F}}-D}^{\varepsilon_{\mathrm{F}}+D} d\varepsilon f_{\mathrm{F}}(\varepsilon)\varepsilon\left[\operatorname{arctanh}\sqrt{\frac{\varepsilon}{\varepsilon_{\mathrm{F}}+D}} - \operatorname{arctanh}\sqrt{\frac{\varepsilon_{\mathrm{F}}-D}{\varepsilon}}\,\right], \end{aligned} \tag{8}$$

where

$$\begin{aligned} g_0(D,q) &= \left((\varepsilon_{\mathrm{F}}-D)^2 - (\varepsilon_{\mathrm{F}}-q)^2\right)\ \operatorname{arctanh}\sqrt{\frac{\varepsilon_{\mathrm{F}}-D}{\varepsilon_{\mathrm{F}}-q}} \\ &\quad + ((\varepsilon_{\mathrm{F}}-D)(\varepsilon_{\mathrm{F}}-q))^{1/2}(D-q)\,, \\ g_1(D,q) &= 4\varepsilon_{\mathrm{F}}D\ \operatorname{arctanh}\sqrt{\frac{\varepsilon_{\mathrm{F}}-D}{\varepsilon_{\mathrm{F}}+D}} - 2D\left(\varepsilon_{\mathrm{F}}^2 - D^2\right)^{1/2}, \\ g_2(D,q) &= \left((\varepsilon_{\mathrm{F}}-q)^2 - (\varepsilon_{\mathrm{F}}+D)^2\right)\ \operatorname{arctanh}\sqrt{\frac{\varepsilon_{\mathrm{F}}-q}{\varepsilon_{\mathrm{F}}+D}} \\ &\quad + (q+D)((\varepsilon_{\mathrm{F}}+D)(\varepsilon_{\mathrm{F}}-q))^{1/2}\,. \end{aligned}$$

The Fermi distribution function f_{F} is constant up to high accuracy for $\varepsilon < \varepsilon_{\mathrm{F}} - D/10$, $\varepsilon > \varepsilon_{\mathrm{F}} + D/10$ in the temperature range $[0.1\mathrm{K}, 10\mathrm{K}]$. Thus we put

$$f_{\mathrm{F}} = \begin{cases} 1 & \text{for} \quad \varepsilon < \varepsilon_{\mathrm{F}} - q \\ 0 & \text{for} \quad \varepsilon > \varepsilon_{\mathrm{F}} + q \end{cases} ,$$

where $q = D/10$.

3. Conclusions

The theoretical impurity specific heat curve of CuCr resulting from 2nd order perturbation theory for the free energy of the s–d exchange Hamiltonian $H_{\mathrm{K}}(M)$ can be adjusted exactly to the experimental one by fitting the temperature dependence of the cutoff $D(T)$ imposed on the s–d exchange $V_{\mathrm{K}}(M)$. $D(T)$ proves to be almost linear in T. A constant D fails to yield agreement with experiment, presumably due to the relatively wide range of temperatures encountered. The theory is therefore no longer a microscopic one. This raises the question of the role of higher order terms of perturbation theory, as well as existence and properties of these terms and $f_2(H_{\mathrm{K}}(M), T)$ in the scaling regime.

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