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BUDAPEST

THE CONTRIBUTION TO THE ELECTRONIC SPECIFIC HEAT DUE TO NEARLY MAGNETIC IMPURITIES

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The change in the effective localized one-electron density of states is estimated for nearly magnetic impurities in the Anderson model and found to explain the unexpectedly high values of $d\gamma/dc$ measured by Aoki and Ohtsuka in AlMn and AlCr alloys assuming 1.6 eV for the width of the virtual level.

The low temperature properties of dilute alloys of iron-group transition metals in aluminum have recently come into the limelight. The problem has been investigated from two different aspects. In the scheme of the Anderson model[1] Rivier and Zuckermann[2] have put forward a theoretical description based on the assumption that in these alloys the transition metal impurities are nearly magnetic. They have shown that the low temperature transport properties[3,4] can satisfactorily be explained in this way. Moreover, the Anderson model provides a natural basis for the description of the charge density distribution measured in NMR measurements[5]. The other theory for these alloys is due to Schrieffer[6]. He supposes that the impurities are magnetic and the non-magnetic behaviour of these alloys is due to the Kondo spin compensated bound state. The basic problem connected with the theoretical description of these alloys, therefore, is whether the condition for the appearance of a localized magnetic moment is fulfilled or not. The fulfilment is closely connected with the order of magnitude of the width of virtual state, Δ, formed at the impurity site. The level widths, determined by Aoki and Ohtsuka[7] from their specific heat measurements using the Hartree-Fock approximation[8,9], would indicate[10] that the localized spin fluctuation model[2] could not be applied for the aluminum based alloys. The purpose of this work is to show that the measured impurity contribution to the electronic specific heat can be explained in the renormalized localized spin fluctuation model using a Δ, which is larger by an order of magnitude than that proposed by Aoki and Ohtsuka.

In the nondegenerate Anderson model[1] the one-impurity problem is described by the Hamiltonian

$$H = \sum_{\underline{k},\sigma} \varepsilon_{\underline{k}\sigma}\, c^{+}_{\underline{k}\sigma}\, c_{\underline{k}\sigma} + \sum_{\sigma} E_d\, d^{+}_{\sigma}\, d_{\sigma} + \sum_{\underline{k},\sigma} \left(V_{kd}\, c^{+}_{\underline{k}\sigma}\, d_{\sigma} + \text{H.C.} \right) + U d^{+}_{\uparrow}\, d_{\uparrow} d^{+}_{\downarrow}\, d_{\downarrow} \,. \qquad /1/$$

Using the commonly accepted approximation

$$\sum_{\underline{k}} \frac{|V_{kd}|^2}{\omega - \varepsilon_{\underline{k}} + i\delta} = i\pi\, |V^2_{kd}|_{av}\, \rho_h(0) = i\Delta \,, \qquad /2/$$

where $\rho_h(0)$ is the density of states of the unperturbed host, in the same way as in the case of interacting fermion systems[11] the low temperature electronic specific heat of a dilute alloy can easily be expressed as

$$C = (\gamma_h + \gamma_i)\, T \qquad /3/$$

Here γ_h is the electronic specific heat coefficient of the unperturbed host, for impurities with nondegenerate levels the impurity contribution, γ_i is given by

$$\gamma_i = c_i\, \frac{\pi^2 k^2}{3} \sum_{\sigma} \frac{1}{\pi}\, \mathrm{Im} \left[G^{R-1}_{d,\sigma}(\omega)\, \frac{\partial G^{R}_{d,\sigma}(\omega)}{\partial \omega} \right]_{\omega = 0 + i\delta} \,. \qquad /4/$$

where c_i is the impurity concentration and $G^{R}_{d,\sigma}(\omega)$ is the Fourier transform of the retarded one-electron Green function at $T = 0$ for the localized d electrons:

$$G^{R}_{d,\sigma}(\omega) = \frac{1}{\omega - E_d - \Sigma_{d,\sigma}(\omega + i\delta) + i\Delta} \qquad /5/$$

If the proper self-energy $\Sigma_{d,\sigma}(\omega)$ is taken in the Hartree-Fock approximation, /4/ yields the well-known result by Klein and Heeger[8] and by Kjöllerström, Scalapino and Schrieffer[9]

$$\gamma_i = c_i\, \frac{\pi^2 k^2}{3} \sum_{\sigma} \rho_{d,\sigma}(0) \,,$$

which can easily be generalized for the case of impurities with degenerate virtual level as

$$\gamma_i = c_i\, \frac{\pi^2 k^2}{3}\, (2\ell + 1) \sum_{\sigma} \rho_{d,\sigma}(0) \,. \qquad /6/$$

Assuming that the transition metal impurities are all non-magnetic in aluminum, Aoki and Ohtsuka[7] have found on the basis of /4/, that the localized one-electron density of states at the Fermi level, $N_{d,\sigma}(0) = 5\rho_{d\sigma}(0) =$ 9.4 eV^{-1}/atom for Al**Mn** and 6.8 eV^{-1}/atom for Al**Cr**.

As in both cases the virtual level is rather close to the Fermi level, $\rho_{d,\sigma}(0) \approx \frac{1}{\pi\Delta}$,this would lead to $\Delta = 0.17$ and 0.23 eV, respectively. These results are an order of magnitude smaller than expected[1]. They would imply[10] that in the Hartree-Fock limit, both the manganese and chromium impurities should be magnetic in aluminum.

We claim that this paradoxical situation simply shows that these impurities in aluminum are rather near to the threshold of being magnetic, as was suggested by Caplin and Rizzuto[3]. Near the magnetic threshold the role of repeated scattering of spin up electrons and spin down holes is pronounced. To take this into account in $\Sigma_d(\omega)$,following Suhl and his coworkers[12, 13, 14] and Rivier, Zuckermann and Sunjic[2], one can use the t-matrix approximation:

$$\Sigma_d(\omega) = \int \frac{d\omega'}{2\pi i}\; t(\omega')\; G_d(\omega'+\omega) \qquad /7/$$

where

$$t(\omega) = U + iU \int \frac{d\omega'}{2\pi} G_d(\omega'+\omega)\, G_d(\omega')\; t(\omega) \equiv U + S(\omega)\, t(\omega)\,. \qquad /8/$$

Here $G_d(\omega)$. is the one-electron Green-function of electrons on the virtual level. /7/, /8/ and the Dyson equation for $G_d(\omega)$ should be solved simultaneously. Using the dominant pole approximation for $t(\omega)$ put forward by Levine et al[13], the direct solution of this system of equations can be got round. In this approximation

$$t(\omega) = \frac{1}{\pi\rho^2_{d,\sigma}(0)} \frac{1}{\Gamma - i\omega} \qquad /\mathrm{Im}\,\omega > 0/; \quad t(z^*) = t^*(z) \qquad /9/$$

where

$$\Gamma = \frac{1 - \mathrm{Re}S(0)}{\pi U \rho^2_{d,\sigma}(0)} \qquad /10/$$

As we shall see later, Γ can be determined from the temperature dependence of the resistivity due to impurities. For a virtual level at the Fermi energy

$$\mathrm{Re}\,\Sigma_d(0) = \mathrm{Im}\,\Sigma_d(0) = \mathrm{Im}\left.\frac{\partial\Sigma_d(\omega)}{\partial\omega}\right|_{\omega=0} = 0\,, \qquad /11/$$

therefore $G_d(\omega+i\delta)$ can be approximated by

$$G_d(\omega+i\delta) \approx \frac{1}{z_1} \frac{1}{\omega + i\Delta/z_1} \qquad /12/$$

where

$$z_1 = \left(1 - \mathrm{Re}\,\frac{\partial\Sigma_d}{\partial\omega}\right)_{\omega=0} \qquad /13/$$

With /12/, /7/ gives

$$\Sigma_d(\omega+i\delta) = \frac{\Delta}{z_1^2}\left[\frac{\omega}{\omega^2 + (\Delta/z_1 - \Gamma)^2}\log\frac{\Delta}{\Gamma z_1} + \right.$$

$$\left. + \frac{\omega+i\Delta/z_1}{(\omega+i\Delta/z_1)^2+\Gamma^2}\log\left(1 - i\frac{z_1\omega}{\Delta}\right) - i\frac{\Delta/z_1}{(\omega+i\Gamma)^2 + (\Delta/z_1)^2}\log\left(1 - \frac{i\omega}{\Gamma}\right)\right]. \qquad /14/$$

Combining the last two equations, one can easily get the following self-consistency condition for the renormalization constant, z_1 :

$$1 - z_1 = \frac{(\Delta/\Gamma)^2}{\Delta/\Gamma - z_1}\left[\frac{z_1}{\Delta/\Gamma - z_1}\log\frac{\Delta}{\Gamma z_1} - 1\right] . \qquad /15/$$

For given values of Δ and Γ , /15/ enables us to determine the renormalization constant. Using this, /4/ gives for a fivefold degenerate level at the Fermi energy

$$N_{d,\sigma\ \mathrm{eff}}(0) = \frac{5z_1}{\pi\Delta} , \qquad /16/$$

which should be measured in the specific heat measurements. The solutions of /15/ for z_1 , at different values of Δ/Γ are given in Table 1. As the closer the impurities to the magnetic threshold, the less the Γ is, one can easily see from Table 1., that approaching the magnetic threshold the enhancement in the impurity contribution to the electronic specific heat becomes more and more pronounced.

Let us show now that the measured temperature dependence of the resistivity[3] and the measured effective density of states[7] determine our parameters, Δ and Γ . As the relaxation time of conduction electrons with energy, ω , measured from the Fermi energy, is given[15] by

$$\tau(T,\omega)^{-1} \sim -|V_{kd}^2|_{av}\ \mathrm{Im}\ G_d\ (T;\ \omega+i\delta) , \qquad /17/$$

the conductivity at low temperatures is

$$\sigma \sim \int \tau(T;\omega)\left(-\frac{\partial f}{\partial\omega}\right)d\omega = \tau(T;0) + \frac{\pi^2(kT)^2}{6}\left.\frac{d^2\tau(T;\omega)}{d\omega^2}\right|_{\omega=0} + \ldots \qquad /18/$$

The reported temperature dependence in resistivity of AlMn and AlCr alloys,

$$\rho(T) = \rho(T=0)\left(1 - T^2/\Theta^2\right) \qquad /19/$$

comes from the temperature dependence of $\mathrm{Im}\ G_d(0)$ and the energy dependence of relaxation time defined in /17/. The former can easily be determined from /7/. Up to the second order in T,

$$\mathrm{Im}\ G_d\ (0+i\delta) = -\frac{1}{\Delta}\left(1 - \frac{\pi^2(kT)^2}{2\Gamma^2}\right) . \qquad /20/$$

Using /17/, /18/ and our approximation for the Green-function /12/, the equation

$$1/\Theta^2 = \pi^2 k^2 \left(\frac{1}{2\Gamma^2} + \frac{z_1^2}{3\Delta^2} \right) \qquad /21/$$

can be derived. According to Caplin and Rizzuto[7] $\Theta = /530 \pm 30/^{\circ}K$ for AlMn and $/1200 \pm 400/^{\circ}K$ for AlCr. As in these cases the host and impurity ions have different masses, as Kagan and Zhernov[16] have shown, another correction can show up in the temperature dependence of resistivity due to the changes in the phonon spectrum. At low temperatures this correction has a leading term, which is also proportional to T^2, but it certainly has positive sign. As we cannot take into account this correction explicitely, we use for Θ the smallest values consistent with the Caplin-Rizzuto measurement, namely $\Theta = 500^{\circ}K$ for AlMn and $\Theta = 800^{\circ}K$ for AlCr. In this way, using /21/, /15/ and /16/, we have found in the case of AlMn alloys that the level with $\Delta = 1.6$ eV gives the measured effective density of states $N_{d,\sigma\ eff}(0) = 9.4\ eV^{-1}/atom$. As the density of states of aluminum[17] is $\rho_h(0) = 0.19\ eV^{-1}/atom$, this value of corresponds to $\left(|V_{kd}|^2_{av}\right)^{N_{1/2}} = 1.65$ eV, which is just of the expected order of magnitude. In this case $\Gamma = 108$ meV is found. If one applies the random phase approximation for $S(\omega)$ defined in /8/, $ReS(0) = U\rho_{d,\sigma}(0)$ is obtained. So, using the values of Δ and Γ obtained, /10/ gives for the effective Coulomb interaction, $U_{eff} = 4.78$ eV, that is rather close to the value found for it by photo-emission measurements in the case of manganese impurities in silver /see e.g. in[10]/.

Now, as to the chromium impurities in aluminum, one can assume that the width of virtual level is approximately the same as in the case of AlMn and it lies near enough to the Fermi energy, so the same procedure can be applied. This way, one gets $N_{d,eff}(0) = 6.4\ eV^{-1}/atom$, which is to be compared with the measured value, $6.8\ eV^{-1}/atom$. The agreement is rather good even in this case.

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Table 1.

The solutions of /15/ for z_1 ,

Δ/Γ	z_1
5	3.7
8	5.5
10	6.7
12	7.8
15	9.6
20	12.6
25	15.5
30	18.5
40	24.3

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