CURIE LAW FOR ANDERSON'S MODEL OF A DILUTE ALLOY*

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The question of the existence of localized magnetic states for Anderson's nondegenerate, extra-orbital model[1] of an impurity in a dilute alloy has been extensively investigated recently.[2-4] Most of this work involved the approximate calculation of Green's functions which were then used to determine the magnetic properties of the impurity.[5] Here we study this model for the case of weak s-d (conduction-band–extra-orbital) mixing, by making a direct expansion of the free energy in powers of the s-d interaction. We find that the susceptibility determined from this expansion of the free energy exhibits a Curie-law behavior at high temperatures. The corrections to this behavior contain a logarithmic divergence at low temperature similar in structure to the perturbation results for the Kondo resistivity anomaly.[6] The sign of this correction reduces the susceptibility below the simple Curie-law value, the reduction becoming larger as the temperature is lowered. We conclude that the nondegenerate Anderson model can exhibit a Curie susceptibility, characteristic of the existence of localized moments, at high temperature if the s-d mixing is weak.[7]

In Anderson's model the impurity is represented by an extra d orbital embedded in an s band of conduction electrons. In the zero-order Hamiltonian we include, besides the single-particle d and conduction-band energies $\epsilon_{ds}=\epsilon_d+\mu Hs$ and $\epsilon_{ks}=\epsilon_k+\mu Hs$, the Coulomb interaction U between two electrons on the d orbital:

$$H_0=\sum_{ks}\epsilon_{ks}n_{ks}+\sum_s\epsilon_{ds}n_{ds}+Un_{d\uparrow}n_{d\downarrow}. \tag{1}$$

Here $s=1$ or -1 for spin $\uparrow$ or spin $\downarrow$, respectively, μ is the Bohr magneton, and H the external magnetic field. The s-d mixing

$$V=\sum_{ks}(V_kC_{ks}{}^{\dagger}C_{ds}+V_k{}^{*}C_{ds}{}^{\dagger}C_{ks}) \tag{2}$$

is treated as a perturbation. Here $n_{ks}=C_{ks}{}^{\dagger}C_{ks}$ and $n_{ds}=C_{ds}{}^{\dagger}C_{ds}$ are the occupation-number operators for the band state of momentum k and spin s and the extra-orbital d state of spin s, respectively. The operators C satisfy the standard anticommutation relations.

Treating V, Eq. (2), as a perturbation, the free energy

$$F=-kT\ln Z \tag{3}$$

can be obtained from the well-known expansion of the partition function

$$Z=\mathrm{Tr}e^{-\beta H_0}[1+\sum_{n=1}^{\infty}\int_0^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2\cdots\int_0^{\lambda_{n-1}}d\lambda_n \times V(\lambda_1)V(\lambda_2)\cdots V(\lambda_n)], \tag{4}$$

where $\beta=1/kT$ and

$$V(\lambda)=e^{\lambda H_0}Ve^{-\lambda H_0}.$$

The susceptibility is then given by

$$\chi=-(\partial^2F/\partial H^2)|_{H=0}. \tag{5}$$

For the case of interest, in which ϵ_d lies below the Fermi level and ϵ_d+U above the Fermi level, the zero-order susceptibility is

$$\chi^{(0)}=\chi_p+\mu^2/kT. \tag{6}$$

Here χ_p is a temperature-independent conduction-band contribution and the second term is the Curie-law contribution of the noninteracting impurity.[8]

The lowest order correction to the free energy is second order in V, and from Eq. (4) one gets

$$F^{(2)}=\sum_{ks}|V_k|^2\left[\frac{f_{ks}n_0}{\epsilon_{ks}-\epsilon_{ds}}+\frac{f_{k-s}n_{ds}}{\epsilon_{k-s}-\epsilon_{d-s}-U}+\frac{(1-f_{ks})n_{ds}}{\epsilon_{ds}-\epsilon_{ks}}+\frac{(1-f_{ks})n_{dd}}{\epsilon_{ds}+U-\epsilon_{ks}}\right]. \tag{7}$$

Here n_0, n_{ds}, and n_{dd} are the zero-order occupation probabilities for zero, single-particle of spin s, and double-particle occupation of the d orbital, respectively,

$$n_0=1/Z_d,\quad n_{ds}=\exp(-\beta\epsilon_{ds})/Z_d,$$

$$n_{dd}=\exp[-\beta(\epsilon_{d\uparrow}+\epsilon_{d\downarrow}+U)]/Z_d,$$

$$Z_d=1+\exp(-\beta\epsilon_{d\uparrow})+\exp(-\beta\epsilon_{d\downarrow})+\exp[-\beta(\epsilon_{d\uparrow}+\epsilon_{d\downarrow}+U)],$$

and $f_{kS}=[\exp(\beta\epsilon_{kS}+1]^{-1}$. Carrying out the momentum sum by assuming a constant density of states $N(0)$ over a bandwidth $\pm W$ about the Fermi energy, and replacing $|V_k|^2$ by an average $|V|^2$, we find

$$F^{(2)}=N(0)|V|^2\sum_s\left\{n_0\ln\left|\frac{\epsilon_{ds}}{W+\epsilon_{ds}}\right|+n_{ds}\ln\left|\frac{\epsilon_{d-s}+U}{W-\epsilon_{d-s}+U}\right|+n_{ds}\ln\left|\frac{\epsilon_{ds}}{W+\epsilon_{ds}}\right|+n_{dd}\ln\left|\frac{\epsilon_{ds}+U}{W+\epsilon_{ds}+U}\right|\right\}. \quad (8)$$

From this,[8] the second-order contribution to χ is

$$\chi^{(2)}=\frac{2\mu^2}{kT}N(0)|V|^2\left(\frac{1}{\epsilon_d}-\frac{1}{\epsilon_d+U}+\frac{1}{W+\epsilon_d+U}-\frac{1}{W+\epsilon_d}\right). \quad (9)$$

If the conduction-band width W is large compared with $|\epsilon_d|$ and ϵ_d+U then the susceptibility correction (9) can be written as

$$\chi^{(2)}=(\mu^2/kT)N(0)J, \quad (10)$$

with an effective antiferromagnetic coupling between the localized orbital and the conduction-band electrons,[9,10]

$$J=2|V|^2U/\epsilon_d(\epsilon_d+U). \quad (11)$$

Continuing the perturbation expansion, the dominant fourth-order contributions involve processes of the type

$$|d\uparrow\rangle\rightarrow|k\uparrow\rangle\rightarrow|d\downarrow\bar{k}'\downarrow k\uparrow\rangle\rightarrow|k\uparrow\rangle\rightarrow|d\uparrow\rangle$$

and

$$|d\uparrow\rangle\rightarrow|k\uparrow\rangle\rightarrow|d\downarrow\bar{k}'\downarrow k\uparrow\rangle\rightarrow|d\downarrow\bar{k}\downarrow d\uparrow\rangle\rightarrow|d\uparrow\rangle.$$

Here hole states are denoted by barred k's. The low-temperature logarithmic singularities to which these processes lead arise from the near energy degeneracy of the initial $|d\uparrow\rangle$ and intermediate $|d\downarrow\bar{k}'\downarrow k\uparrow\rangle$ states when the particle $k\uparrow$ and hole $k'\downarrow$ are close to the Fermi surface. Carrying out the λ integrations in (4), we find for these processes

$$F^{(4)}\sim\sum_{kk'}|V_k|^2|V_{k'}|^2\left(\frac{1}{\epsilon_d-\epsilon_k}-\frac{1}{\epsilon_d+U+\epsilon_{k'}}\right)^2\left(\frac{(1-f_{k\uparrow})f_{k'\downarrow}n_{d\uparrow}}{\epsilon_{d\uparrow}-\epsilon_{d\downarrow}-\epsilon_{k\uparrow}+\epsilon_{k'\downarrow}}+\frac{(1-f_{k\downarrow})f_{k'\uparrow}n_{d\downarrow}}{\epsilon_{d\downarrow}-\epsilon_{d\uparrow}-\epsilon_{k\downarrow}+\epsilon_{k'\uparrow}}\right). \quad (12)$$

In the important region where k and k' are near the Fermi surface, the first bracketed term in (12) is simply $J^2/4$. Making this substitution and carrying out the k and k' sums, we find to logarithmic accuracy

$$F^{(4)}\sim[-(\mu H)^2/2kT][N(0)J]^2\ln(kT/W) \quad (13)$$

and

$$\chi^{(4)}\sim-(\mu^2/kT)[N(0)J]^2\ln(kT/W). \quad (14)$$

Combining these results, Eqs. (6), (10), and (14), the susceptibility is

$$\chi\sim\chi_p+(\mu^2/kT)\{1+N(0)J+[N(0)J]^2\ln(kT/W)\}. \quad (15)$$

Here J is given by (11), $N(0)$ is the unperturbed single-particle conduction-electron density of states, and W is an effective bandwidth. In higher order there are selected processes which, in perturbation theory, contribute to χ terms of the form $(\mu^2/kT)N(0)J[N(0)J\ln(kT/W)]^n$. It appears that these terms can be represented by writing[11]

$$\chi\sim\chi_p+\frac{\mu^2}{kT}\left[1+\frac{N(0)J}{1-N(0)J\ln(kT/W)}\right]. \quad (16)$$

Since J is negative, this perturbation result fails to converge when kT is less than $W\exp[1/N(0)J]$. Before this temperature is reached the paramagnetic contribution to χ changes sign and the expression (16) gives an unphysical result. Here we are primarily interested in the high-temperature region where the straight perturbation result, Eq. (15), is appropriate. It is clear that in this region the nondegenerate Anderson model exhibits a Curie-law behavior characteristic of a localized moment.

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[1]P. W. Anderson, Phys. Rev. 124, 41 (1961).

[2]J. R. Schrieffer and D. C. Mattis, Phys. Rev. 140, A1412 (1965).

[3]A. C. Hewson and M. J. Zuckermann, Phys. Letters 20, 219 (1966).

[4]B. Kjöllerström, D. J. Scalapino, and J. R. Schrieffer, to be published.

[5]The behavior of the Green's functions for low frequencies, measured relative to the Fermi energy, is particularly important in obtaining the correct magnetic behavior. The approximate truncation procedure used in Ref. 3 fails to account adequately for this behavior and leads to erroneous magnetic predictions.

[6]J. Kondo, Progt. of Theoret. Phys. (Kyoto) 32, 37 (1964).

[7]This behavior of the Anderson model was suggested by P. W. Anderson, J. Appl. Phys. 37, 1194 (1966).

[8]We assume through this work that $|\epsilon_d|$ and ϵ_d+U are much greater than kT.

[9]This effective antiferromagnetic coupling, implicit in the Anderson model, was first pointed out by P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. 6, 124 (1961).

[10]J. R. Schrieffer and P. A. Wolff have recently shown that the Anderson model can be transformed to a form similar to that of the s-d exchange model used by Kondo, Ref. 6. They find an effective exchange coupling which reduces to Eq. (11) for electron scattering near the Fermi surface.

[11]A similar result for the s-d exchange model has been obtained by K. Yosida and A. Okiji, Progt. Theoret. Phys. (Kyoto) 34, 504 (1965), using Rayleigh-Schrödinger perturbation theory.

EXPERIMENTAL DETERMINATION OF E-k RELATIONSHIP IN ELECTRON TUNNELING*

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We report here measurements of electron tunneling through thin AlN films in which the imaginary component of the propagation vector in the forbidden band has been determined as a function of energy from the dependence of the tunneling current upon insulator thickness. The relationship so derived agrees well with Franz's empirical relationship[1] for a material with the 4.2-eV forbidden-band energy of AlN. These results allow the prediction of voltage-current characteristics over the entire range of experimental variables with no arbitrary adjustable parameters, and also subject to several internal self-consistency checks. In each case complete consistency is observed. To the authors' knowledge, this represents the first unambiguous demonstration of such consistency in thin-film tunneling.

AlN films were made by treatment of freshly evaporated Al films in a N_2 glow discharge at a pressure of 200 μ for 3 min. Mg counter electrodes were subsequently evaporated through a mask. The entire procedure is similar to that used for Al_2O_3 samples.[2] Measurements made at room, liquid-nitrogen, and liquid-helium temperatures gave essentially identical results.

Previously, current-voltage data have been interpreted by fitting the observed characteristic of a structure with a particular insulator thickness to a theoretical model which assumed the dependence of k, the imaginary component of the propagation vector in the insulator forbidden band, on E, the energy below the conduction-band edge, to be given by

$$E = h^2k^2/2m_i^*. \tag{1.1}$$

The entire behavior of electron tunneling is dominated by the exponential attenuation of the electron wave function in the forbidden gap of the insulator. Hence a detailed understanding of the process can only come when the energy-dependent attenuation coefficient k of the wave function is known accurately. By far the most direct and unambiguous method of obtaining the value of k is by the variation of the current density as a function of insulator thickness.

In the case where (1) the tunneling current I per unit area can be considered as proportional to the product of the tunneling probability and an effective number of electrons within one of the metals incident on the barrier presented by the insulator per unit area per second with energies near the metal Fermi level and with transverse momenta near zero, and (2) the barrier can be considered as trapezoidal, then, for low voltages, I is linear with applied voltage V and is given by[3]

$$I = A(V/x)\exp[-2\bar{k}(0)x], \tag{1.2}$$

where $\bar{k}(0)$ is the average value of k encountered