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Energy and Specific Heat Due to an Impurity Atom in a Dilute Alloy

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The ground-state energy for the Anderson model of an impurity atom in a paramagnetic host metal is evaluated as a function of the impressed magnetic moment. Within the Hartree-Fock approximation we find that the ground-state energy has an absolute minimum for a finite value of the magnetic moment, corresponding to a stable localized magnetic moment. When correlations are included within the low-density approximation, the energy has its minimum for vanishing magnetic moment and the system cannot magnetize, in agreement with the results of Schrieffer and Mattis. The expression for the ground-state energy is extended to nonzero temperature and the specific heat due to the dilute impurities is calculated. It is shown that the anomalous specific heat derived by Anderson within the Hartree-Fock approximation is spurious.

INTRODUCTION

The many-electron correlations associated with the formation and stability of localized magnetic moments on solute atoms in dilute alloys are only partially understood at present. Theories for localized magnetic states have been developed by Anderson,[1] Wolff,[2] and Clogston.[3] Anderson has introduced a model in which the impurity atom is represented by an extra d orbital immersed in the s-band states of the host. This state is broadened into a virtual level in the sense discussed by Friedel.[4] The broadening is caused by a one-body s-d interaction (scattering matrix element) which mixes the d state with the band states. The Coulomb interaction U of opposite spin electrons occupying the d orbital is the only two-body interaction taken into account and, with the s-d mixing, generates the many-electron correlations of this model. In Anderson's original discussion these correlations were investigated by means of a self-consistent Hartree-Fock calculation, and a stability condition for the existence of localized moments was obtained along with a determination of the susceptibility and specific-heat contributions of these correlations. Recently Schrieffer and Mattis[5] have investigated the effects of correlations beyond Hartree-Fock. A stability criterion based upon the occurrence of a singularity in the susceptibility was shown to give the Anderson conditions within the Hartree-Fock approximation. It is known, however, that correlations between electrons of opposite spin, neglected in the Hartree-Fock approximation, are important. For the case in which the virtual level is located with respect to the Fermi level so that it contains only a small fraction of a particle (or a hole) the important correlations can be taken into account by introducing a two-particle (-hole) t matrix. Schrieffer and Mattis showed that in this low-density[6] limit the susceptibility is always finite, independent of the strength of the Coulomb interaction U. This is in contrast with the Hartree-Fock result which predicts that for sufficiently large U the susceptibility will become singular and beyond this a local moment will be stable. This is another example of the fact that the Hartree-Fock approximation can overestimate the strength of the effective exchange interaction.

In this paper, the ground-state energy for the Anderson model of a dilute alloy is investigated. By introducing an external magnetic field, it is possible to study the energy associated with the many-electron correlations as a function of the magnetization M of the d orbital. If the minimum energy occurs for a finite value of M, then a local moment will be stable. Within the Hartree-Fock approximation we show that the criterion for the occurrence of such a minimum is just that deduced by Anderson and corresponds to a singularity in the susceptibility. In the low-density[6] case, Schrieffer and Mattis showed that the energy has a local minimum at zero magnetization (i.e., the susceptibility does not become singular). Here we show that *no subsidiary minimum* occurs and therefore there is no localized moment. It was in fact just this question of the possibility of a subsidiary energy minimum at nonvanishing values of M corresponding to a metastable or stable magnetic phase, which prompted this investigation. The occurrence of a stable subsidiary minimum would have far reaching consequences indicating the necessity of a bootstrap approach in which the presence of a local moment would have to be assumed at the start of the calculation in order to determine the onset criterion for such a moment.

Generalizing this work to nonzero temperature, we derive an expression for the energy associated with the impurities. Using this, the specific heat due to the

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[2] P. A. Wolf, Phys. Rev. **124**, 1030 (1961).

[3] A. M. Clogston, Phys. Rev. **125**, 439 (1962); **136**, A1417 (1964).

[4] J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).

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

[6] Here low density refers to a small particle (or hole) occupation of an impurity d state and not to the concentration of impurities, which we always assume is sufficiently dilute so that impurity-impurity correlations can be neglected.

impurities is calculated. The anomalous term obtained and discussed by Anderson is shown to be spurious. The expression which we obtain agrees with some experimental results on dilute alloys of Ni in Be.[7] Here the impurity atoms have a low hole concentration and therefore the low-density t-matrix approximation should be valid. Within this approximation, theory predicts that there are no stable localized moments and none are observed in the dilute alloys of Ni in Be.

The following discussion is divided into three parts: In the first section, an exact expression for the ground-state energy for the Anderson model of a dilute alloy is constructed. The energy is given in terms of an integral over the single-particle d-state Green's function. In the second section, we evaluate this expression using forms obtained for the Green's function in the self-consistent Hartree-Fock approximation and the low-density t-matrix approximation. In the Hartree-Fock case, Anderson's results are reproduced and plots of the ground-state energy as a function of magnetization are given for a range of d-state level position and level width parameters. In the low-density t-matrix case we do not find a stable or metastable magnetic state. This supports the conclusion of Schrieffer and Mattis that the Hartree-Fock solution, which predicts a moment in the large-U limit, is qualitatively in error for the low-density case. In the final section, an exact expression for the energy at nonzero temperature is derived and used to calculate the specific heat.

EXACT EXPRESSIONS FOR THE GROUND-STATE ENERGY

In Anderson's model, one assumes that the band states of the host metal can be treated as independent quasiparticles characterized by a momentum index k, a spin index s and an energy ϵ_{ks}. In the presence of a z-directed magnetic field H_z, the band-state energy is $\epsilon_{ks}=\epsilon_k-s\lambda$ where $s=\pm1$ and $\lambda=\mu H_z$, μ being the Bohr magneton. We consider the system of the band electrons and a single impurity atom. The impurity is introduced as an extra localized orbital of energy $\epsilon_{ds}=\epsilon_d-s\lambda$, which is mixed with the band states by a matrix element V_{kd}. All two-body Coulomb interactions are neglected except the Coulomb interaction U between opposite-spin electrons on the localized orbital. Using $c^\dagger$ and c as the Fermi creation and destruction operators, the Hamiltonian for this system is

$$H=\sum_{ks}\epsilon_{ks}n_{ks}+\sum_{s}\epsilon_{ds}n_{ds}+\sum_{ks}(V_{kd}c_{ks}{}^\dagger c_{ds}+\text{H.c.})+Un_{d+}n_{d-},$$

where

$$n_{ks}=c_{ks}{}^\dagger c_{ks},\quad\text{and}\quad n_{ds}=c_{ds}{}^\dagger c_{ds}. \tag{1}$$

We wish to write down an expression for the ground-state energy in terms of the single-particle propagator for the extra orbital

$$G_{dd}{}^{(s)}(t)=-i\langle0|Tc_{ds}(t)c_{ds}{}^\dagger(0)|0\rangle. \tag{2}$$

Our subsequent analysis is then based upon the evaluation of this ground-state-energy expression using several approximate forms for $G_{dd}{}^{(s)}$.

In order to relate the ground-state energy to the propagator (2), we consider the commutation relations

$$[c_{ks},H]=\epsilon_{ks}c_{ks}+V_{kd}c_{ds}, \tag{3}$$

and

$$[c_{ds},H]=\epsilon_{ds}c_{ds}+\sum_k V_{dk}{}^*c_{ks}+Uc_{ds}n_{d,-s}. \tag{4}$$

In terms of these commutators the Hamiltonian can be written

$$H=\sum_s\Big\{\sum_k c_{ks}{}^\dagger[c_{ks},H]+\tfrac{1}{2}c_{ds}{}^\dagger[c_{ds},H]+\tfrac{1}{2}\epsilon_{ds}n_{ds}+\tfrac{1}{2}\sum_k V_{dk}{}^*c_{ds}{}^\dagger c_{ds}\Big\}. \tag{5}$$

Now it is convenient to introduce the four one-particle Green's functions defined by

$$G_{ij}{}^{(s)}(t)=-i\langle0|Tc_{is}(t)c_{js}{}^\dagger(0)|0\rangle, \tag{6}$$

where i and j stand for indices k or d, and $|0\rangle$ is the true ground state of the system. The ground-state energy is simply related to these Green's functions. From the equation of motion for the operators c_{ks} we get

$$\langle0|c_{ks}{}^\dagger[c_{ks},H]|0\rangle=\frac{d}{dt}G_{kk}{}^{(s)}(t)\Big|_{t=0}, \tag{7}$$

or taking Fourier transforms

$$\langle0|c_{ks}{}^\dagger[c_{ks},H]|0\rangle=\frac{1}{2\pi i}\int_c\omega G_{kk}{}^{(s)}(\omega)d\omega, \tag{8}$$

where C is the contour consisting of the real axis and a semicircle at infinity in the upper half plane. In the same way we get the relations

$$\langle0|c_{ds}{}^\dagger[c_{ds},H]|0\rangle=\frac{1}{2\pi i}\int_c\omega G_{dd}{}^{(s)}(\omega)d\omega, \tag{9}$$

$$\langle0|n_{ds}|0\rangle=\frac{1}{2\pi i}\int_c G_{dd}{}^{(s)}(\omega)d\omega, \tag{10}$$

$$\langle0|c_{ds}{}^\dagger c_{ks}|0\rangle=\frac{1}{2\pi i}\int_c G_{kd}{}^{(s)}(\omega)d\omega. \tag{11}$$

Now we have expressed the expectation value of the terms in the Hamiltonian (5) as certain integrals of Green's functions. However these Green's functions are not independent, but coupled to each other through the s-d interaction V. From the equations of motion we get

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[7] A. P. Klein and A. J. Heeger, Phys. Rev. **144**, 458 (1966).

the following relations:

$$\omega G_{kd}{}^{(s)}(\omega)=\epsilon_{ks}G_{kd}{}^{(s)}(\omega)+V_{kd}G_{dd}{}^{(s)}(\omega)\,, \tag{12}$$

$$\omega G_{kk'}{}^{(s)}(\omega)=\delta_{kk'}+\epsilon_{ks}G_{kk'}{}^{(s)}(\omega)+V_{kd}G_{dk'}{}^{(s)}(\omega)\,. \tag{13}$$

Elimination gives

$$G_{kd}{}^{(s)}(\omega)=[V_{kd}/(\omega-\epsilon_{ks})]G_{dd}{}^{(s)}(\omega)\,, \tag{14}$$

and

$$G_{kk}{}^{(s)}(\omega)=\frac{1}{\omega-\epsilon_{ks}}+\frac{|V_{kd}|^2}{(\omega-\epsilon_{ks})^2}G_{dd}{}^{(s)}(\omega)\,. \tag{15}$$

We also introduce the one-body self-energy $S^{(s)}(\omega)$ given by

$$S^{(s)}(\omega)=\sum_k\frac{|V_{kd}|^2}{\omega-\epsilon_{ks}}\,. \tag{16}$$

Thus we can write the ground-state energy

$$\langle 0|H|0\rangle=\frac{1}{2\pi i}\sum_s\int_c\left\{\sum_k\omega G_{dd}{}^s(\omega)+\frac{\omega+\epsilon_{ds}+S^{(s)}(\omega)}{2}G_{dd}{}^{(s)}(\omega)\right\}d\omega\,. \tag{17}$$

As in Anderson's analysis we can neglect the real part of the self-energy S since it primarily leads to a level shift which can be taken care of by a redefinition of ϵ_{ds}. Furthermore we assume the self-energy to be spin-independent, and take

$$S^{(s)}(\omega)=-i\Gamma\ \mathrm{sgn}\omega\,,$$

where

$$\Gamma=\pi N(0)|V_{kd}|_{\mathrm{av}}{}^2\,.$$

Here we have assumed that the density of states in the s band varies slowly and replaced it by its value at the Fermi surface $N(0)$. In this approximation we can write

$$\frac{1}{2\pi i}\int_c\sum_k\omega G_{kk}{}^{(s)}(\omega)d\omega$$

$$=\frac{1}{2\pi i}\int_c\left(\sum_k\frac{\omega}{\omega-\epsilon_{ks}}-G_{dd}{}^{(s)}(\omega)\omega\frac{\partial}{\partial\omega}S(\omega)\right)d\omega$$

$$=\sum_{k\leqslant k_F}\epsilon_{ks}=\mathrm{const}\,,$$

since $\omega\partial S(\omega)/\partial\omega$ is of the form $\omega\delta(\omega)$. Neglecting this constant we have

$$E=\langle 0|H|0\rangle=\frac{1}{2\pi i}\sum_s\int_c\frac{\omega+\epsilon_{ds}+S(\omega)}{2}G_{dd}{}^{(s)}(\omega)d\omega\,. \tag{18}$$

Taking $G_0{}^{(s)}(\omega)^{-1}=\omega-\epsilon_{ds}-S(\omega)$ we define a proper Coulomb self-energy by the Dyson equation

$$G_{dd}{}^{(s)}(\omega)=G_0{}^{(s)}(\omega)+G_0{}^{(s)}(\omega)\Sigma^{(s)}(\omega)G_{dd}{}^{(s)}(\omega)\,. \tag{19}$$

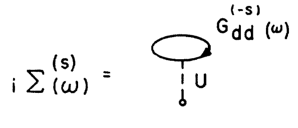

FIG. 1. Hartree-Fock approximation of the self-energy.

With this relation, Eq. (18) can be rewritten in a form which will be useful in the subsequent analysis

$$E=\frac{1}{2\pi i}\sum_s\int_c(\omega-\tfrac{1}{2}\Sigma^{(s)}(\omega))G_{dd}{}^{(s)}(\omega)d\omega\,. \tag{20}$$

EVALUATION OF THE GROUND-STATE ENERGY

Hartree-Fock Approximation

In the Hartree-Fock approximation the self-energy $\Sigma^{(s)}(\omega)$ is given by

$$\Sigma^{(s)}(\omega)=\frac{U}{2\pi i}\int_c G_{dd}{}^{(-s)}(\omega)d\omega=Un_{-s}\,, \tag{21}$$

corresponding to the diagram shown in Fig. 1. Thus we can write the Green's function

$$G_{dd}{}^{(s)}(\omega)=1/(\omega-E_s+i\Gamma\ \mathrm{sgn}\omega)\,, \tag{22}$$

where

$$E_s=\epsilon_{ds}+\Sigma^{(s)}(\omega)=\epsilon_d-s\lambda+Un_{-s}\,, \tag{23}$$

and n_s is the expectation value of n_{ds}, given by

$$n_s=\frac{1}{2\pi i}\int_c d\omega G_{dd}{}^{(s)}(\omega)=\frac{1}{\pi}\cot^{-1}\left(\frac{E_s}{\Gamma}\right)\,. \tag{24}$$

The ground-state energy (20) is now

$$E=\frac{1}{2\pi i}\sum_s\int_c\{\omega-\tfrac{1}{2}Un_{-s}\}G_{dd}{}^{(s)}(\omega)d\omega\,. \tag{25a}$$

Folding the contour as in Fig. 2, and rewriting, we have

$$E=\frac{1}{\pi}\sum_s\int_{-\infty}^{0}\omega\,\mathrm{Im}G_{dd}{}^{(s)}(\omega)d\omega-Un_+n_-\,. \tag{25b}$$

To make the integral convergent we only perform the integration from a cutoff energy, the contribution from which we consider as a constant and neglect. Doing this the energy can be written

$$E=\sum_s\epsilon_{ds}n_s+Un_+n_-+\sum_s\frac{\Gamma}{2\pi}\ln\frac{E_s{}^2+\Gamma^2}{\Gamma^2}\,. \tag{25c}$$

To evaluate the energy from this expression we must

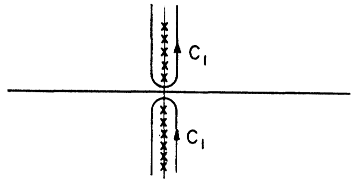

FIG. 2. Cut structure of the Green's functions and the contour C.

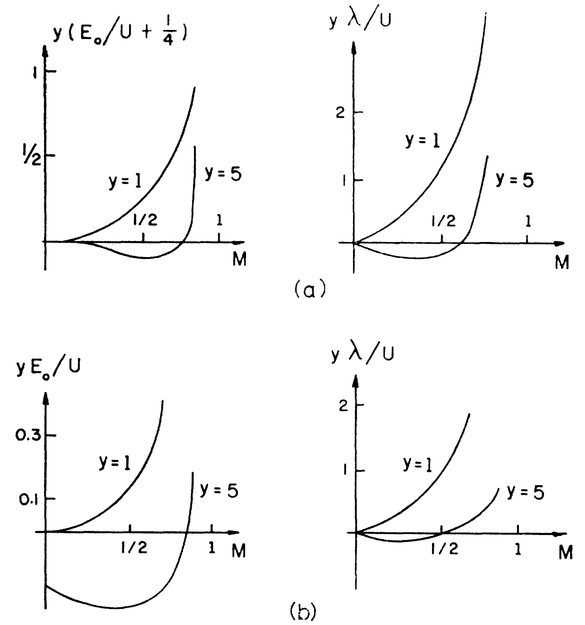

FIG. 3. Curves of yE_0/U and $y\lambda/U$ for: (a) $-\epsilon_d/U=\frac{1}{2}$, and (b) $-\epsilon_d/U=\frac{1}{4}$. $y=U/\Gamma$.

solve the Eqs. (24) self-consistently for n_s and use these values in (25c). In this way we find the ground-state energy as a function of the chemical potential μ, the external magnetic field H_z, the impurity level position ϵ_d, the strength of the Coulomb repulsion U and the strength of the s-d scattering Γ. The value of the chemical potential is set by the host metal.

In order to investigate the magnetic behavior of this system, it is useful to study that part of the ground-state energy which is not associated with the coupling to the external field H_z. This is given by

$$E_0=E+\mu MH_z. \qquad (26)$$

Here μM is the magnetic moment caused by the d electrons and

$$M=n_+-n_-. \qquad (27)$$

By using Eqs. (24) and (26) with H_z as a parametric variable, we can study E_0 as a function of the magnetization M for various values of the parameters ϵ_d, U and Γ. If E_0 has a minimum for a finite value of M, we conclude that the system will have a localized moment. Note that the introduction of H_z is merely a formal device, since in any laboratory field the magnetic energy $-H_zM\mu$ is negligible compared to U and Γ. As an illustration we have carried through this graphically for four different cases, namely $-\epsilon_d/U=\frac{1}{4}$ and $\frac{1}{2}$, $U/\Gamma=1$ and 5. In Fig. 3 we give E_0 as a function of M and also the magnetic field as function of M.

We can get a bit more insight into the behavior of the ground-state energy as a function of M by rephrasing the problem slightly. Using Eqs. (24) we eliminate E_s from Eq. (25) which gives

$$E=\sum_s\left\{\epsilon_{ds}n_s-\frac{\Gamma}{\pi}\ln\sin\pi n_s\right\}+Un_+n_-. \qquad (28)$$

Denoting the total number of electrons on the impurity by $N=n_++n_-$, the energy can be written

$$E=\epsilon_dN-\lambda M-\frac{\Gamma}{\pi}\ln\tfrac{1}{2}(\cos\pi M-\cos\pi N)+\tfrac{1}{4}U(N^2-M^2). \qquad (29)$$

Here N and M should be viewed as certain functions of λ, ϵ_d, U and Γ. As E is the ground-state energy, it is stable to variations in N and M. Hence they are determined from the requirements

$$\partial E/\partial N=0 \quad\text{and}\quad \partial E/\partial M=0. \qquad (30)$$

Taking ϵ_d, U and Γ as fixed, these equations give the variation of E, N, and M with respect to the applied magnetic field.

It is, however, more interesting to take the magnetization M as independent variable. We are interested in the internal part of the ground-state energy E_0 which does not depend on the external field as a function of M in the interval $0\leq M\leq 1$. The variation of E_0 with magnetization is

$$\frac{\partial E_0}{dM}=\frac{\partial E_0}{\partial\lambda}\frac{\partial\lambda}{\partial M}+\frac{\partial E_0}{\partial N}\frac{\partial N}{\partial M}+\frac{\partial E_0}{\partial M}. \qquad (31)$$

Using Eqs. (26), (29), and (30), we find

$$dE_0/dM=\Gamma[\sin\pi M/(\cos M-\cos\pi N)]-\tfrac{1}{2}UM. \qquad (32)$$

It follows from Eq. (29) that E_0 is an even function of M tending to + infinity as $M\rightarrow N$, and to a finite value as $M\rightarrow 0$. Furthermore, the curvature of the derivative is positive since

$$\frac{\partial^3E_0}{\partial M^3}=\pi^2\Gamma\frac{2-(\cos\pi M-\cos\pi N)\sin\pi M\cos\pi N}{(\cos\pi M-\cos\pi N)^3}\geqslant 0. \qquad (33)$$

This means that E_0 can have at most one extremum which has to be a minimum. Consequently, if and only if the sign of the derivative at the origin is negative, a minimum will occur.

For small values of M,

$$dE_0/dM=M(\tfrac{1}{2}\Gamma\pi[1/\sin^2(\tfrac{1}{2}\pi N)]-\tfrac{1}{2}U). \qquad (34)$$

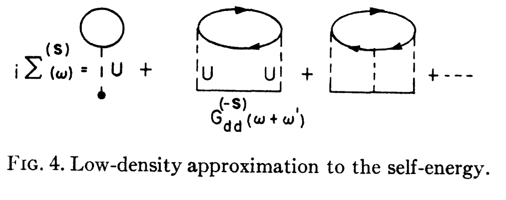

FIG. 4. Low-density approximation to the self-energy.

The condition for a localized moment in the Hartree-Fock approximation is therefore that

$$(U/\Gamma\pi)\sin^2(\tfrac{1}{2}\pi N)>1. \qquad (35)$$

This is the same as Anderson's condition.

In the special case $-\epsilon_d/U=\frac{1}{2}$, we find that Eqs. (30) can be solved analytically giving $N=1$ and

$$E_0=U\left\{-\tfrac{1}{4}-\tfrac{1}{4}M^2-\frac{2\Gamma}{\pi U}\ln\cos(\tfrac{1}{2}\pi M)\right\}, \qquad (36)$$

$$\lambda=dE_0/dM=U\left\{-\tfrac{1}{4}M+\frac{\Gamma}{U}\tan(\tfrac{1}{2}\pi M)\right\}. \qquad (37)$$

Within the Hartree-Fock approximation the occurrence of a minimum in E_0 at finite M is simply related to the sign of the curvature $\partial^2E_0/\partial M^2$ at $M=0$. Also it is related to the sign of the weak-field magnetic susceptibility χ, as can be seen from the following argument. For small M we can write

$$E=-H_z\mu M+aM^2+0(M^3).$$

Equation (30) then gives

$$\mu H_z=2aM+0(M^2),$$

or

$$a=\mu H_z/2M=\mu^2/2\chi.$$

Hence we can write generally for small M

$$E_0=(\mu^2/2\chi)M^2.$$

Thus we see from the small-M limit that the criterion for the appearance of a local moment is associated with χ changing sign. In the vicinity of the magnetic threshold χ exhibits a simple pole $[1-(U/\pi\Gamma)\sin^2(\frac{1}{2}\pi N)]^{-1}$ and switches from $+\infty$ to $-\infty$.

CORRELATION EFFECTS

If the impurity has a small number of electrons (or holes) occupying the d level ($\Gamma/E\ll1$), the correlations are predominantly 2-particle since higher particle correlations are suppressed by increasing powers of the effective number of particles Γ/E. In this case, as discussed by Schrieffer and Mattis, the two-body contributions to the self-energy can be obtained from the diagrams of Fig. 4. In this approximation, the self-energy is

$$\Sigma^{(s)}(\omega)=\frac{1}{2\pi i}\int_c t(\omega+\omega')G_{dd}{}^{(-s)}(\omega')d\omega'. \qquad (38)$$

Here the t matrix is given by

$$t(\omega)=U/[1+U\phi(\omega)] \qquad (39)$$

with

$$\phi(\omega)=\frac{1}{2\pi i}\int G_{dd}{}^{(+)}(\omega+\omega')G_{dd}{}^{(-)}(-\omega')d\omega'. \qquad (40)$$

Schrieffer and Mattis showed that the zero-field susceptibility remains positive (and finite) in the low-density limit, independent of the strength of U. This behavior of the zero-field susceptibility does not rule out the possibility that a localized moment exists in the low-density approximation. To investigate this, it is necessary to determine the behavior of the ground-state energy as a function of the magnetization. A subsidiary minimum could exist at a finite value of M and not be reflected by the behavior of the zero-field susceptibility which senses only the behavior of the energy in the region of small magnetization. Here we will present results for the low-density approximation which show that the ground-state energy is a monotonically increasing function of M so that no localized moment can occur.

In order to solve Eqs. (38) and (40) self-consistently we approximate (38) by

$$\Sigma^{(s)}(\omega)=U_{\text{eff}}n_{-s}, \qquad (41)$$

where

$$U_{\text{eff}}=U/[1+U\phi(0)]. \qquad (42)$$

Using this self-energy in the Green's functions we find

$$\phi(0)=\frac{1}{\pi(E_++E_-)}\left(\arctan\frac{E_+}{\Gamma}+\arctan\frac{E_-}{\Gamma}\right), \qquad (43)$$

where E_s is now defined as

$$E_s=\epsilon_d-s\lambda+U_{\text{eff}}n_{-s}.$$

The number of electrons is the solution to the coupled equations,

$$n_s=(1/\pi)\cot^{-1}(E_s/\Gamma). \qquad (44)$$

With the help of this expression $\phi(0)$ can be rewritten in the following way

$$\phi(0)=\frac{1-N}{2\Gamma}\,\frac{\cos\pi M-\cos\pi N}{\sin\pi N}. \qquad (45)$$

Substituting this expression into Eq. (42) we find how the effective potential depends on N and M. As in the Hartree-Fock case we are interested in the ground-state energy in the absence of an external magnetic field. Taking U_{eff} instead of U in Eq. (29) this energy is

$$E_0=\epsilon_dN-(\Gamma/\pi)\ln\tfrac{1}{2}(\cos\pi M-\cos\pi N)$$
$$+\tfrac{1}{4}(N^2-M^2)U/[1+U\phi(0)]. \qquad (46)$$

In the same way as before from Eq. (31) we have

$$\frac{1}{\Gamma}\frac{dE_0}{dM}=\frac{\sin\pi M}{\cos\pi M-\cos\pi N}-\tfrac{1}{2}M\frac{U/\Gamma}{1+U\phi(0)}$$
$$+\frac{N^2-M^2}{4}\left(\frac{U/\Gamma}{1+U\phi(0)}\right)^2\left(-\Gamma\frac{\partial\phi(0)}{\partial M}\right). \qquad (47)$$

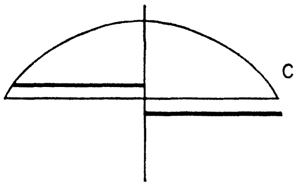

FIG. 5. Cut and poles of $E(T)$.

Neglecting the last term in Eq. (47) which is positive and noting that $U/[1+U\phi(0)]\leqslant 1/\phi(0)$ it follows that

$$\frac{1}{\Gamma}\frac{dE_0}{dM}\geqslant\frac{\sin\pi M}{\cos\pi M-\cos\pi N}-\frac{M}{2\Gamma\phi(0)}$$
$$=\frac{M}{\cos\pi M-\cos\pi N}\left\{\frac{\sin\pi M}{M}-\frac{\sin\pi N}{1-N}\right\}. \quad (48)$$

In the low-density limit the total number of d electrons (holes) is small, say $N<\frac{1}{2}$ ($N>\frac{3}{2}$). Thus we find that E_0 always has a positive derivative for positive M, and the only minimum that can occur is for $M=0$. Consequently a subsidiary minimum cannot exist and within the low-density approximation there is no localized moment.

THE SPECIFIC HEAT

In order to determine the impurity contribution to the specific heat, we calculate the energy associated with the presence of an impurity at nonzero temperatures. Using the standard imarinary-time Green's-function techniques, Eq. (20) goes over to

$$E(T)=kT\sum_{sn}\left(i\omega_n-\tfrac{1}{2}\Sigma^{(s)}(i\omega_n)\right)G_{dd}{}^{(s)}(i\omega_n). \quad (49)$$

By writing this as a contour integral, Fig. 5, we get

$$E(T)=-\sum_s\frac{1}{2\pi i}\int_c G_{dd}{}^{(s)}(\omega)\left(\omega-\tfrac{1}{2}\Sigma^{(s)}(\omega)\right)\times f(\omega)d\omega, \quad (50)$$

where $f(\omega)$ is the Fermi function

$$f(\omega)=[e^{\omega/kT}+1]^{-1}.$$

By deforming the contour so that it runs just above and just below the cut along the real axis, we find

$$E(T)=-\sum_s\int_{-\infty+i\delta}^{+\infty+i\delta}f(\omega)\times\frac{1}{\pi}\operatorname{Im}\{G_{dd}{}^{(s)}(\omega)\left(\omega-\tfrac{1}{2}\Sigma^{(s)}(\omega)\right)\}d\omega. \quad (51)$$

We are interested in evaluating this for situations in which only the real part of Σ is important (e.g., Hartree-Fock approximation). In this case Eq. (51) can be simply written as an integral over the spectral weight

$$A^{(s)}(\omega)=-\frac{1}{\pi}\operatorname{Im}G_{dd}{}^{(s)}(\omega), \quad (52)$$

and if Σ_1 denotes the real part of Σ we have for the energy per impurity

$$E(T)=\sum_s\int_{-\infty}^{+\infty}A^{(s)}(\omega)\left(\omega-\tfrac{1}{2}\Sigma_1{}^{(s)}(\omega)\right)f(\omega)d\omega. \quad (53)$$

The above form clearly exhibits the energy as the weighted average of ω where the weight is the average occupation $f(\omega)$ times the effective density of states $A(\omega)$. The term $-\frac{1}{2}\Sigma(\omega)$ prevents double counting the two-particle interaction energy. This term just *cancels* the anomalous specific-heat contribution discussed by Anderson.

To perform the integration in (53) we make use of the formula

$$\int_{-\infty}^{+\infty}g(\omega)f(\omega)=\int_{-\infty}^{\mu(T)}g(\omega)d\omega+\frac{\pi^2k^2T^2}{6}\left.\frac{dg}{d\omega}\right|_{\omega=0}, \quad (54)$$

where $\mu(T)$ is the temperature-dependent part of the chemical potential. Terms of order T^3 and higher are neglected. In the following we assume that $\mu(T)$ is proportional to T^2. Thus we have

$$E(T)=\sum_s\left\{\int_{-\infty}^{\mu(T)}A^{(s)}(\omega)(\omega-\tfrac{1}{2}Un_{-s})d\omega+\frac{\pi^2k^2T^2}{6}\times\left(A^{(s)}(0)-\tfrac{1}{2}Un_{-s}\left.\frac{\partial A^{(s)}(\omega)}{\partial\omega}\right|_{\omega=0}\right)\right\}. \quad (55)$$

The contribution to the specific heat C from the impurity is $C=\partial E/\partial T$ so that neglecting terms of order T^2 we have

$$C=\sum_s\left\{\frac{\partial\mu}{\partial T}A^{(s)}(0)(-\tfrac{1}{2}Un_{-s})+\int_{-\infty}^{0}\left((\omega-\tfrac{1}{2}Un_{-s})\frac{\partial A^{(s)}}{\partial T}-\tfrac{1}{2}A^{(s)}(\omega)U\frac{\partial n_{-s}}{\partial T}\right)d\omega+\frac{\pi^2k^2T}{3}\left(A^{(s)}(0)-\tfrac{1}{2}Un_{-s}\left.\frac{\partial A^{(s)}(\omega)}{\partial\omega}\right|_{\omega=0}\right)\right\}. \quad (56)$$

In the same way as Eq. (53) was obtained, it follows that the average number of d electrons at temperature T is given by

$$n_s=\int A^{(s)}(\omega)f(\omega)d\omega, \quad (57)$$

Taking the derivative with respect to temperature and using Eq. (54), we obtain to order T^2.

$$\frac{\partial n_s}{\partial T}=\int_{-\infty}^{0}\frac{\partial A^{(s)}(\omega)}{\partial T}d\omega+\frac{\partial\mu}{\partial T}A^{(s)}(0)+\frac{\pi^2k^2T}{3}\frac{\partial A^{(s)}(\omega)}{\partial\omega}\bigg|_{\omega=0}. \tag{58}$$

From the definition of the spectral weight function Eq. (52) we find that the temperature dependence is contained in the self-energy Σ_1. Assuming that this does not depend on the frequency, we have

$$\frac{\partial A^{(s)}}{\partial T}=-\frac{\partial A^{(s)}}{\partial\omega}\frac{\partial\Sigma_1{}^{(s)}}{\partial T}. \tag{59}$$

Making a partial integration we can write

$$\int_{-\infty}^{0}\omega\frac{\partial A^{(s)}}{\partial T}=n_s\frac{\partial\Sigma_1{}^{(s)}}{\partial T}. \tag{60}$$

Rearranging terms using Eqs. (58), (59), and (60) the specific heat is

$$C=\sum_s\left\{\frac{\pi^2k^2T}{3}A^{(s)}(0)+\tfrac{1}{2}\left(n_s\frac{\partial\Sigma_0{}^{(s)}}{\partial T}-\frac{\partial n_s}{\partial T}\Sigma_1{}^{(s)}\right)\right\}. \tag{61}$$

Here the first term on the right-hand side of Eq. (61) is just the ordinarily expected contribution. Making the Hartree-Fock approximation for Σ, we now show that the remaining terms vanish. In the Hartree-Fock approximation we simply have $\Sigma^{(s)}=Un_{-s}$ and the assumption that Σ is independent of ω made in (59) is valid. Inserting this expression for the self-energy into Eq. (61) we obtain

$$C=\tfrac{1}{3}\pi^2k^2T\textstyle\sum_s A^{(s)}(0). \tag{62}$$

Thus in the Hartree-Fock approximation the specific-heat contribution associated with the impurities shows no irregularities and depends simply on the density of states at the Fermi surface. A measurement of the specific heat will therefore give information about the increase in the density of states due to the added d state. See (6).

CONCLUSION

The essential results of the above analysis are:

(1) If one treats Anderson's extra-orbital model of an impurity in a dilute alloy within the Hartree-Fock (HF) approximation, the energy of the system plotted as a function of magnetization M has a minimum at $M=0$ for $A(0)U<1$, and at a nonzero value of M for $A(0)U>1$, where $A(0)$ is the density of states of the self-consistently determined virtual level without spin polarization evaluated at the Fermi surface. The value of M at the minimum is in agreement with that found by Anderson by solving the HF equations.

(2) If one treats correlation effects for the above model in the low-density limit, the energy has a minimum at $M=0$, regardless of the size of U, and is a monotonically increasing function of $|M|$, having no subsidiary minima. This result completes the discussion of Schrieffer and Mattis regarding the absence of a localized moment, in Anderson's model at low temperature, in a treatment which includes correlation effects in the low-density limit.

(3) A correct treatment within the Hartree-Fock approximation of the specific heat C associated with the impurity does not give rise to the anomalous term obtained by Anderson. Rather, one finds the intuitive result,

$$C=\tfrac{1}{3}\pi^2k^2T\textstyle\sum_s A^{(s)}(0),$$

where $A^{(s)}(0)$ is the density of states of the self-consistently determined virtual level for spin orientation s evaluated at the Fermi surface.

The above results are in agreement with the recent experiments of Klein and Heeger[7] on Ni in Be.

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