GROUND-STATE AND LOW-TEMPERATURE PROPERTIES OF PARAMAGNETIC IMPURITIES IN METALS

Joel A. Appelbaum and Jun Kondo*
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 15 August 1967)

The ground state of a paramagnetic impurity recently proposed by Kondo is studied both variationally and with perturbation theory. It is shown that the ground state is stable to perturbations from the nondiagonal part of the Hamiltonian. In addition, the low-temperature properties of the system are obtained.

It has recently been shown[1-3] that the ground-state energy of the antiferromagnetic exchange Hamiltonian contains a nonanalytic function of the exchange coupling J. This nonanalytic part (n.a.p.) was first found by Nagaoka,[4] who identified it with the "binding energy" of the electron-spin-polarization cloud which in his solution formed around the localized spin.

This physical picture of "spin compensation" was exploited by Kondo[1] and Yosida,[2] among others[3] who proposed variational ground states with singletlike configurations for the electrons and localized spins.

In this Letter we study a ground state proposed by Kondo[1] variationally and with perturbation theory to show that it is stable with respect to perturbations. In addition, the low-temperature properties of the system are studied.

We follow the notation of Kondo.[1] The exchange Hamiltonian is

$$\mathcal{H}=\sum_{\vec{k},s}\epsilon_{\vec{k}}a_{\vec{k}s}^{\dagger}a_{\vec{k}s}+\frac{|J|}{N}\sum_{\substack{\vec{k},\vec{k}'\\ s,s'}}a_{\vec{k}s}^{\dagger}a_{\vec{k}'s'}\vec{S}\cdot\vec{\sigma}_{ss'}, \quad (1)$$

where $a_{\vec{k}s}$ is the destruction operator for an electron with energy $\epsilon_{\vec{k}}$, momentum $\vec{k}$, and spin s in a band of width $2D$ and density ρ. $\vec{S}$ is the localized spin and $\vec{\sigma}$ the Pauli matrices; $J<0$. We take $S=\frac{1}{2}$.

The variation function assumed is

$$\Psi=2^{-1/2}(a_{0-}^{\dagger}\alpha-a_{0+}^{\dagger}\beta)\prod_{l}a_{l+}^{\dagger}a_{l-}^{\dagger}|\mathrm{vac}\rangle, \quad (2)$$

where α and β are the usual state vectors for spin $\frac{1}{2}$.

Furthermore,

$$a_{0s}^{\dagger}=\sum_{\vec{k}}C_{0\vec{k}}a_{\vec{k}s}^{\dagger};\quad a_{ls}^{\dagger}=\sum_{\vec{k}}C_{l\vec{k}}a_{\vec{k}s}^{\dagger}, \quad (3)$$

and

$$\sum_{\vec{k}}C_{n\vec{k}}^{\dagger}C_{n'\vec{k}}=\delta_{nn'}\quad (n,n' \text{ including } 0). \quad (4)$$

The average energy is

$$E=2\sum_{l}^{\mathrm{Occ}}\sum_{\vec{k}}|C_{l\vec{k}}|^2\epsilon_{\vec{k}}+\sum_{\vec{k}}|C_{0\vec{k}}|^2\epsilon_{\vec{k}}-\frac{3|J|}{2N}\Big|\sum_{\vec{k}}C_{0\vec{k}}\Big|^2. \quad (5)$$

Varying $C_{l\vec{k}}$ subject to (4), we find

$$C_{l\vec{k}}=\mu_l C_{0\vec{k}}/2(\epsilon_{\vec{k}}-\lambda_l), \quad (6)$$

where μ_l and λ_l, Lagrange multipliers, are determined by (4).

Substituting $C_{l\vec{k}}$ into (5) one obtains E as a functional of $C_{0\vec{k}}$, from which a nonlinear integral equation for $C_{0\vec{k}}$ can be obtained.[5]

The essential feature of C_{0k} reflected in the integral equation we exhibit through the Ansatz

$$C_{0k}=\frac{(\epsilon/2\rho)^{1/2}}{|\epsilon_k|+\epsilon}, \quad (7)$$

where ϵ is a parameter later to be identified with the n.a.p. of the energy. This Ansatz for C_{0k} completes our definition of the unitary transformation between $a_k^{\dagger}$ and $a_n^{\dagger}$, and after some manipulations, we can now write our Hamiltonian as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2, \quad (8)$$

$$\mathcal{H}_0=\sum_{l,s}\lambda_l a_{ls}^{\dagger}a_{ls}+\frac{|J|}{N}f_0^2 a_{0s}^{\dagger}a_{0s'}\vec{S}\cdot\vec{\sigma}_{ss'}, \quad (9)$$

$$\mathcal{H}_1=\frac{|J|}{N}\sum_{\substack{l,l'\\ s,s'}}f_l^{*}f_{l'}a_{ls}^{\dagger}a_{l's'}\vec{S}\cdot\vec{\sigma}_{ss'}, \quad (10)$$

$$\mathcal{H}_2=\sum_{l,s,s'}T_{s,s'}(l)(a_{ls}^{\dagger}a_{0s'}+a_{0s}^{\dagger}a_{ls'}), \quad (11)$$

where

$$f_n = \sum_{\vec{k}} C_{n\vec{k}}, \tag{12}$$

$$T_{ss'}(l) = \frac{|J|}{N} f_0 f_l \vec{S}\cdot\vec{\sigma}_{ss'} + \tfrac{1}{2}\mu_l \delta_{ss'}. \tag{13}$$

Studying $\mathcal{H}$, we find that Ψ is an eigenstate of $\mathcal{H}_0$ with energy $E(\epsilon)$, and that ϵ, determined variationally from $E(\epsilon)$, is[6]

$$\epsilon = De^{-1/3|J|\rho}, \tag{14}$$

for which

$$E(\epsilon) = 2\sum_{k<k_F} \epsilon_k - \epsilon.$$

Further, $\mathcal{H}_1$, when treated by perturbation theory, reproduces the usual analytic part of the ground-state energy. This follows essentially by inspection from the properties of f_l, e.g., $f_l \to 1$ for $\lambda_l > \epsilon$ and $f_l \to 0$ for $\lambda_l \to 0$.

We see quite clearly that ϵ represents the difference in energy between the perturbation state and our new ground state.

Finally, we find that for the ϵ given in (14), $(a_{ls}^\dagger a_{0s'} + a_{0s}^\dagger a_{ls'})T_{ss'}(l)|\psi\rangle \cong 0$, $\lambda_l > \epsilon$, from which one can show that all the terms in the energy resulting from perturbation theory in $\mathcal{H}_2$ are of higher order $(J\rho)$ in ϵ than those coming from $\mathcal{H}_0$. A similar conclusion has been drawn for the terms involving both $\mathcal{H}_2$ and $\mathcal{H}_1$, insofar as these terms have been studied.

The above precedure has also been followed for ferromagnetic coupling $(J>0)$ and triplet coupling for Ψ. All the conclusions above are the same,[7] but now

$$\epsilon_t = De^{-1/J\rho} \quad (J>0). \tag{15}$$

We conclude that there appears to exist for both signs of the exchange coupling essentially new ground states unobtainable from the usual perturbation theories.

The low-temperature properties $(T<\epsilon)$ of this new ground state have been studied[8] by appropriately generalizing $C_{0\vec{k}}$ to finite temperature via

$$C_{0\vec{k}} \propto 1/\{[1-2f(\epsilon_{\vec{k}})]\epsilon_{\vec{k}} + \epsilon(T)\}, \tag{16}$$

where $F(\epsilon_{\vec{k}})$ is the Fermi function and $\epsilon(T)$ the now temperature-dependent "binding energy" to be determined variationally from the free energy.

We find for the specific heat

$$C_V \propto T\ln(\epsilon_0/T), \quad T<\epsilon, \tag{17}$$

where $\epsilon_0 = \epsilon(T=0)$.

The phase shifts for the scattering states a_{ls} have been obtained and from them the resistivity ρ calculated. We quote here the results when potential scattering V is presented in addition to exchange scattering.[5,8,9]

The total phase shift as a function of energy λ and temperature T is

$$\delta(\lambda, T) = \delta_V + \tfrac{1}{2}\pi - \frac{4\lambda}{\pi\tilde{\epsilon}(T)}\ln\frac{|\lambda|+2T}{\tilde{\epsilon}(T)}, \tag{18}$$

where

$$\tilde{\epsilon}(T) = \tilde{\epsilon}_0 + \frac{32}{3\pi^2}\frac{T^2}{\tilde{\epsilon}_0}\ln\frac{T}{\tilde{\epsilon}_0}, \tag{19}$$

$$\tilde{\epsilon}_0 = D\exp\{-(3|J|\rho\cos^2\delta_V)^{-1}\}, \tag{20}$$

and δ_V is the phase shift due to potential scattering alone.

The resistivity is[10]

$$\rho' = \rho_0'\left[\cos^2\delta_V - \frac{16}{3}\cos 2\delta_V\left(\frac{T}{\tilde{\epsilon}(T)}\ln\frac{T}{\tilde{\epsilon}(T)}\right)^2\right], \tag{21}$$

where ρ_0' is a constant. Note that ρ' may increase or decrease with temperature depending on the δ_V.

We would like to thank P. W. Anderson and L. Dworin for valuable discussions.

---

*On leave of absence from Electro-technical Laboratory, Tanashi, Tokyo, Japan.

[1]J. Kondo, Progr. Theoret. Phys. (Kyoto) 36, 429 (1966).

[2]K. Yosida, Phys. Rev. 147, 223 (1966).

[3]K. Yosida and H. Miwa, Phys. Rev. 144, 375 (1966); K. Yosida, Progr. Theoret. Phys. (Kyoto) 36, 875 (1966); A. J. Heeger and M. A. Jensen, Phys. Rev. Letters 18, 488 (1967).

[4]Y. Nagaoka, Phys. Rev. 138, A1112 (1965).

[5]J. A. Appelbaum and J. Kondo (to be published).

[6]The ϵ found here is the same as previously found by Kondo (Ref. 1), and is larger than that predicted from various perturbation-theoretic, self-consistent, or variational-type calculations done to date, with the exception of a variational calculation for the Anderson model by P. W. Anderson (to be published).

[7]The method has also been applied to ordinary potential scattering. In lowest order, e.g., $\mathcal{H}_0$, one finds a nonzero ϵ; however, consideration of higher order terms yields, as it should, no anomalous binding energy.

[8]J. Kondo and J. A. Appelbaum (to be published).

[9]The importance of including potential scattering for the resistivity has been emphasized by K. Fischer, Phys. Rev. 158, 613 (1967) (see also references contained therein), and J. Kondo (to be published).

[10]It is interesting to note that the predicted temperature dependence of the resistivity, e.g., that a plot of $[1-\rho'(T)/\rho'(T=0)]^{1/2}/T$ vs $\ln T$ yields a straight line, is consistent with the following two experiments: the resistivity in Cu with 0.05% Fe reported by J. P. Frank, F. D. Manchester, and D. L. Martin [Proc. Roy. Soc. (London) A263, 494 (1961)] between 4.0 and 14°K, and the resistivity in Ir with 0.5% Fe found by M. P. Sarachik [Bull. Am. Phys. Soc. 12, 348 (1967) and Phys. Rev. (to be published)] in the temperature range 1.4-38°K. The slope of the straight line is the only free parameter; unfortunately it is determined as a function of of both ϵ_0 and δ_V, as can be seen from (21), so that ϵ_0 and δ_V are not fixed by it separately.

OBSERVATION OF SPIN WAVES IN ERBIUM

A. D. B. Woods, T. M. Holden,* and B. M. Powell
Physics Division, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada
(Received 31 July 1967)

The energy/wave vector spin-wave dispersion relation, $\hbar\omega(\vec{q})$, for the a and c directions in erbium metal in its conical magnetic phase has been measured at 4.2°K using inelastic neutron scattering. We believe these measurements are the first observations of short-wavelength spin waves in such a structure. The results indicate that the anisotropy energy is much greater than the exchange energies and that the interplanar exchange energies along the c axis are of oscillating sign as required for the stability of the structure of the spiral component. This behavior is very different from that found by Møller and Houmann[1] for ferromagnetic terbium where succeeding interplanar exchange terms had the same sign.

Below 20°K erbium has a conical magnetic structure[2] with a cone angle θ of about 28.5° and a spiral wave vector $\vec{k}_0$ of $(0, 0, 2\pi/4.1c)$, where c is the lattice spacing along the hexagonal axis.

The experiments were carried out using the Chalk River triple-axis spectrometer in its constant-$\vec{Q}$ mode of operation.[3] The crystal was oriented so that the a and c axes were in the scattering plane. Measurements were made along the c axis ($[00\zeta]$ direction) between the reciprocal lattice points (001) and (003) and along four lines parallel to the a axis ($[\zeta\zeta 0]$) passing through the reciprocal lattice positions (002), (001), $(0, 0, 2-k_0c/2\pi)$, and $(0, 0, 1+k_0c/2\pi)$.

The measured spin-wave dispersion curves are shown in Fig. 1. Since there are two atoms in each unit cell the dispersion relation consists of both an optic and an acoustic branch. In the $[00\zeta]$ direction these are continuous at the zone boundary and are shown as a single branch in a double-sized zone. The observed spin-wave energies do not go to zero[4] at $\vec{q}=\vec{k}_0$ but have a finite value for all $\vec{q}$. Furthermore the observed neutron distributions consisted of single groups instead of the three which, in principle, should be present[5,6]; in fact, if the specimen consists of different magnetic domains, six distinct branches should be observable. Both the apparent absence of a zero-frequency mode and the observation of only one neutron group result from the smallness of the cone angle θ.

For $\theta = 28.5°$, neutron groups corresponding to four of these six modes are at least an order of magnitude less intense than those corresponding to the other two, while the splitting in energy between these latter two is too small to be resolved under the present experimental conditions. Even for small θ the neutron groups associated with the $q=0$ modes increase rapidly in intensity as $\omega \to 0$ but they cannot readily be resolved from the very intense

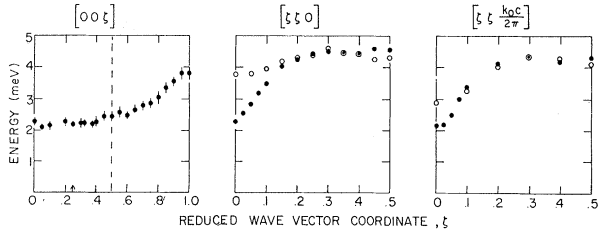

FIG. 1. The spin-wave dispersion curves of erbium measured at 4.2°K. The wave-vector coordinates are measured from the nuclear reciprocal lattice points. Error bars have been omitted for the a axis measurements but, on the average, are ~4%. Note that for the c direction the flatness of the initial half of the branch results in a negative sign for the large second Fourier component. The small arrow indicates the magnetic satellite position on the c axis.