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DEMAGNETIZATION THROUGH LEVEL CROSSING: THE EFFECT OF CHARGE FLUCTUATIONS *

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We have studied the effect of charge fluctuations on the behviour of a magnetic impurity in a metal, by applying the functional integral method to the Anderson model. In the high correlation limit, as the distance from the impurity level to the Fermi level is varied, we obtain a progressive demagnetization of the impurity.

1. Introduction

The functional integral method has been extensively applied [1,5] to the study of the Anderson model [6]. This method, which was originally introduced by Stratonovich and Hubbard [7] consists of replacing the electrostatic interaction of the two electrons at the impurity site by a time-dependent field acting on the localized electrons. This field has to be averaged with a Gaussian weight to obtain the partition function.

A second possibility is to introduce two fields ξ and η acting, respectively, on the spin density $n_\uparrow - n_\downarrow$ and on the charge density $n_\uparrow + n_\downarrow$. In this paper, we present results obtained within this two field method. As happens with the functional integral method, one must resort to approximations in order to obtain results beyond formal solutions. We have worked within the static approximation, in which the fields ξ and η are time-independent. It can be shown that this method gives exact results in two limiting cases: finite electrostatic repulsion U and vanishing width Γ or finite width Γ and no electrostatic repulsion.

In order to get manageable expressions one usually applies the extremal approximation on the η field [2, 4,5]. As is known, this implies a neglect of the fluctuations associated with this field. This approach has been critized by Bari [8] on the grounds that, although higher in energy [2], charge fluctuations are strictly non-vanishing at $T \neq 0$ and their neglect leads to the wrong partition function as $\Gamma \to 0$.

For this reason we have tried to improve on the extremal approximation by taking the value of η, or equivalently choosing the value of the charge density, that makes the free energy an extremun for each value of the ξ field. This is an adiabatic mean of including the charge fluctuations. Proper considerations of the stochastic nature of these fluctuations [9] would in fact require to include the high frequency components of the η field in the spirit of the RPA′ [1], for instance. This approach will be the subject of a forthcoming paper.

We have studied the behaviour of the static magnetic susceptibility as the energy of the localized level is varied. In real systems, this parameter may be governed by pressure [10] or alloying, as is probably the case for Ce impurities in a La-Th matrix [11]. It is seen that the susceptibility goes from a Curie law in the symmetric case to a temperature independent form as the level moves relative to the Fermi level.

2. Functional integral scheme

We start by considering the Anderson Hamiltonian [6] which is given by:

$$H = H_0 + H_1 ,$$

$$H_0 = \sum_{k\sigma} \epsilon_k C^+_{k\sigma} C_{k\sigma} + \sum_{\sigma} E_\sigma b^+_\sigma b_\sigma + \sum_{k\sigma} (V_{kd} C^+_{k\sigma} b_\sigma$$

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$$+ V_{kd}^{*} b_{\sigma}^{+} C_{k\sigma}) , \quad (1)$$

$$H_1 = U n_{\uparrow} n_{\downarrow} ; n_{\sigma} = b_{\sigma}^{+} b_{\sigma} ,$$

where we have used the usual notation. H_1 could be rewritten in the following form:

$$H_1 = \tfrac{1}{4} U[(n_{\uparrow} + n_{\downarrow})^2 - (n_{\uparrow} - n_{\downarrow})^2] . \quad (2)$$

Now, a straightforward application of the Stratanovich–Hubbard method [7] gives for the partition function

$$Z = \int \mathrm{d}\xi(\tau)\, \mathrm{d}\eta(\tau)\, Z(\xi, \eta) \exp\{-\Pi \int_0^1 [\xi(\tau)^2 + \eta(\tau)^2] \times \mathrm{d}\tau\} , \quad (3)$$

where

$$Z(\xi, \eta) = \mathrm{tr}\, T \exp\{-\beta \int_0^1 H(\tau)\, \mathrm{d}\tau\} = \rho(\xi, \eta) , \quad (4.a)$$

$$H(\tau) = H_{0\tau} - \sum_{\sigma} \frac{C}{\beta} Z_{\sigma}(\tau)\, \eta_{\sigma}(\tau) , \quad (4.b)$$

τ is a fictitious time, T the time ordered operator for τ, ρ the density matrix, and

$$z_{\sigma}(\tau) = \sigma\xi(\tau) + \mathrm{i}\eta(\tau); C = \sqrt{\pi\beta U} . \quad (4.c)$$

If we call

$$\beta\Omega(\xi, \eta) = \Pi \int_0^1 [\xi(\tau)^2 + \eta(\tau)^2]\, \mathrm{d}\tau - \ln Z(\xi, \eta) , \quad (5)$$

the value of $\eta(\tau)$ which makes this "free energy" extremal is given by

$$\frac{\partial\beta\Omega(\xi, \eta)}{\partial\eta(\tau)} = 0 = 2\Pi\eta(\tau) - \mathrm{i}C \frac{\mathrm{tr}\, T[\sum_{\sigma} \eta_{\sigma}(\tau)\, \rho(\xi, n)]}{\mathrm{tr}\, T\rho(\xi, \eta)} . \quad (6)$$

So we have for these stationary paths

$$\eta(\tau) = \frac{\mathrm{i}C}{2\Pi} \langle n_{\uparrow}(\tau) + n_{\downarrow}(\tau)\rangle . \quad (7)$$

In his original paper on functional integrals, Hubbard [7] proved that the stationary paths are "time-independent" (those given by (6) and $[\partial\beta\Omega(\xi, \eta)/\partial\xi(\tau)] = 0$); and that the above conditions correspond to the evaluation of the original partition function in the Hartree approximation.

In most of the literature, the results refer to the case where $n = \langle n_{\uparrow}(\tau) + n_{\downarrow}(\tau)\rangle = 1$ [5]. Since we are interested in cases where the occupation of the localized level changes, we calculate it in a selfconsistent way for each $\xi(\tau)$. This leads us to take

$$\eta = \frac{\mathrm{i}C}{2\Pi} n . \quad (8)$$

Replacing this value in the expression for Z and following the method of ref. [1], we rewrite this expression using a coupling parameter λ and define:

$$Z(\lambda) = \int \mathrm{d}\xi(\tau)\, Z(\xi, n, \lambda) \exp\left\{-\Pi \int_0^1 \xi(\tau)^2 \mathrm{d}\tau + \frac{C^2 n^2}{4\Pi}\right\} , \quad (9a)$$

$$Z(\xi, n, \lambda) = \mathrm{tr}\, T \exp\{-\beta \int_0^1 (H_{0\tau} + \lambda\Pi(\xi, n))\, \mathrm{d}\tau\} , \quad (9b)$$

$Z(\lambda = 1)$ is the physical partition function. As was shown in ref. [1], one has the formal result:

$$\frac{Z(\xi, n, \lambda = 1)}{Z(\lambda = 0)} = \exp[\sum_{\sigma} \mathrm{tr} \ln(1 - k^{\sigma})] , \quad (10)$$

where $Z(\lambda = 0) = Z_0$ is the partition function of the $U = 0$ problem, and we have used the Fourier transform of the $\xi(\tau)$ field:

$$\xi(\tau) = \sum_{\nu=-\infty} \xi_{\nu} e^{-\mathrm{i}\Omega_{\nu}\tau} ; \Omega_{\nu} = 2\Pi\nu ; \xi_{\nu} = \xi_{-\nu}^{*} ,$$

$$K_{nm}^{\sigma} = \frac{C z_{\sigma(n-m)}}{\mathrm{i}\omega_n - \beta E_{\sigma} + \mathrm{i}\beta\Gamma_n} , \quad (11)$$

where $z_{\sigma}(n - m) = \sigma\xi_{n-m} - (Cn/2\Pi)\delta_{nm}$; $\omega_n = (2n + 1)\Pi$ and $\Gamma_n = \Gamma$ sign n, with $\Gamma = \Pi D(0) \langle|V_{kd}|^2\rangle_{\mathrm{av}}$. The expression for Z is:

$$Z = \int_{-\infty}^{\infty} \mathrm{d}\xi_0 \prod_{\nu>0} \int 2\mathrm{d}^2\xi_{\nu} \exp\left\{-\Pi\left[\sum_{\nu} |\xi_{\nu}|^2 - \left(\frac{Cn}{2\Pi}\right)^2\right] + \sum_{\sigma} \mathrm{tr} \ln(1 - K^{\sigma})\right\} , \quad (12a)$$

where $\int \mathrm{d}^2\xi_{\nu}$ denotes the integral over the complex ξ_{ν}

plane. At this point, we make the static approximation; that is, we neglect all non-zero frequencies in the Fourier transform field ξ_ν. The partition function reduces to:

$$\frac{Z_{st}}{Z_0} = \int_{-\infty}^{\infty} d\xi_0 \exp\left\{-\Pi\left[\xi_0^2 - \left(\frac{Cn}{2\Pi}\right)^2\right] + \sum_{\sigma n} \ln\left[1 + \frac{CZ_\sigma(0)}{i\omega_n - \beta E_\sigma + i\Gamma_n}\right]\right\}. \qquad (12b)$$

The n-sum can be evaluated (see Keiter (1970) [3] and is found to be:

$$\sum_{\sigma n} (\ln)\left(1 + \frac{CZ_\sigma(0)}{i\omega n - \beta E_\sigma + i\beta\Gamma_n}\right) = -\frac{C^2 n}{2\Pi} + \sum_\sigma (\ln) \frac{\bar{\Gamma}(\frac{1}{2} + \beta\Gamma/2\Pi - i\beta E_\sigma/2\Pi)}{\bar{\Gamma}(\frac{1}{2} + \beta\Gamma/2\Pi - i[\beta E_\sigma - CZ_\sigma(0)]/2\Pi}, \qquad (13a)$$

where $\bar{\Gamma}$ denotes the gamma function. For $\beta\Gamma >> 1$, it further reduces to:

$$= \frac{C^2 n}{2\Pi} + \frac{\beta}{\Pi} \sum_\sigma \left\{[E_\sigma - CZ_\sigma(0)] \arctan\left(\frac{E_\sigma - CZ_\sigma(0)}{\Gamma}\right) - \frac{1}{2} E_\sigma \arctan\left(\frac{E_\sigma}{\Gamma}\right) - \frac{1}{2}\Gamma \ln\left[\left(\frac{E_\sigma - CZ_\sigma(0)/\beta}{\Gamma}\right)^2 + 1\right] + \frac{1}{2}\Gamma \ln\left[\left(\frac{E_\sigma}{\Gamma}\right)^2 + 1\right]\right. . \qquad (13b)$$

In this approximation, the self-consistent expression (7) to obtain n is:

$$1 - n = \frac{1}{\Pi} \sum_\sigma \arctan\left[\frac{E_\sigma - \sigma C\xi_\sigma/\beta + C^2 n/2\Pi\beta}{\Gamma}\right]. \qquad (14)$$

We rewrite (12b) in the form

$$\frac{Z_{st}}{Z_0} = \int_{-\infty}^{\infty} d\xi_0 \exp[-\beta\tilde{\Omega}(\xi_0)] . \qquad (12b)$$

To study the "free-energy" $\tilde{\Omega}(\xi_0)$, for different values of the parameters:

$$\beta(\xi_0) = \Pi\xi_0^2 - \frac{C^2}{2\Pi} n\left(\frac{n}{2} - 1\right) - \frac{\beta}{\Pi} \sum_\sigma \left\{(E_\sigma - \sigma C\xi_0/\beta + C^2 n/2\Pi) \arctan\left[\frac{E_\sigma - \sigma C\xi_0/\beta + C^2 n/2\Pi\beta}{\Gamma}\right] - \frac{1}{2}\Gamma \ln\left[\left(\frac{E_\sigma - \sigma C\xi_0/\beta + C^2 n/2\Pi\beta}{\Gamma}\right)^2 + 1\right]\right\} . \qquad (15)$$

We drop terms independent of ξ_0 and n since they do not change the results.

We confine ourselves to the study of the high correlation limit. Defining two dimensionless parameters $u = U/\Pi\Gamma$, $\epsilon = E/U$, we study the behaviour of the free energy at high u. The results are indicated in fig. 1, which gives $\beta\Omega$ as a function of ξ, for two different values of u and different values of ϵ. For the

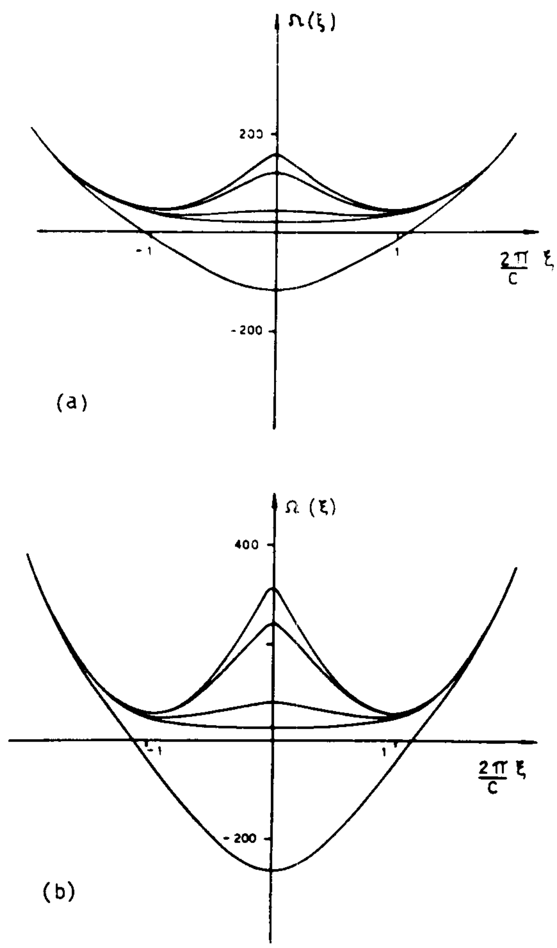

Fig. 1. Effective free energy as a function of ξ, in arbitrary units, in the two fields approach, for different values of parameter; (a) $u = 10$; (b) $u = 20$. In both figures we have from top to bottom: $\epsilon = -\frac{1}{2}, -\frac{1}{4}; -\frac{1}{20}, 0, \frac{1}{4}$.

symmetric case ($\epsilon = -\frac{1}{2}$), we reobtain the usual form of the free energy (in this case $n = 1$ for all ξ_0) with two minima at $\xi_0 = \pm C/2\Pi$.

As the impurity level approaches the Fermi energy, the maximum at $\xi = 0$ moves down. Thus the barrier between the two minima tends to disappear, a fact that increases the probability of the non-magnetic states which finally dominate the free energy when the level gets sufficiently close to the Fermi energy.

Because of the electron-hole symmetry, the results depend only on $|\epsilon + \frac{1}{2}|$.

If a single gaussian field is used, which couples to the spin density [1], and the static approximation is used, the corresponding functional free energy is given by

$$\beta\widetilde{\Omega}(\xi) = \Pi\xi^2 - \frac{\beta}{\Pi}\sum_\sigma \left(E_\sigma + U/2 - \sigma C\xi/\beta \times \arctan\left(\frac{E_\sigma + U/2 - \sigma C\xi/\beta}{\Gamma}\right) - \frac{1}{2}\Gamma \ln\left[\left(\frac{E_\sigma + U/2 - \sigma C\xi/\beta}{\Gamma}\right)^2 + 1\right]\right), \tag{16}$$

where now $C = \sqrt{2\Pi\beta U}$. The corresponding form of $\beta\widetilde{\Omega}(\beta)$ as a function of ξ is given in fig. 2. As the impurity level approaches the Fermi level, we see that in this case there is a tendency of the minima at $|\xi| = C/2\Pi$ to persist, so that they give a strong magnetic contribution even for $\epsilon = 0$.

We see from the analytic form for $\beta\widetilde{\Omega}(\xi)$ that the results for a single gaussian field are similar to those of the two field case if we set there $n = 1$. This shows the importance of considering the variation of impurity occupation in dealing with the magnetic behaviour of the system. In the next section, we consider the magnetic susceptibility.

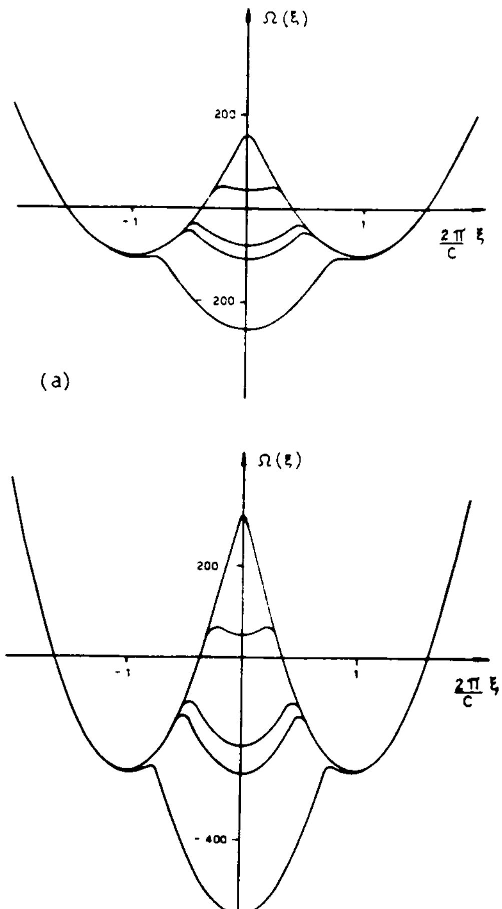

Fig. 2. Effective free energy as a function of ξ, in arbitrary units, for a single Gaussian field. The values of ϵ are the same as in fig. 1: (a) $u = 10$; (b) $u = 20$.

Magnetic susceptibility

We now turn to the evaluation of the static excess susceptibility, which, in a quite general way, is defined by:

$$\Delta\chi = -\frac{1}{\beta}\left(\frac{\partial^2}{\partial h^2}\ln(Z/Z_0)\right)_{h=0}, \tag{17}$$

where h is the magnetic field applied in the Z direction. Since the Zeeman energy enters additively with ξ_0 in the general (12a), one can shift ξ_0 to $\xi_0 + \beta\mu h/C$ (μ = Bohr magneton), and this yields the expression:

$$\Delta\chi = \frac{2\Pi^2}{U}\left[2\Pi\langle\xi_0^2\rangle - 1\right]. \tag{18}$$

Here $\langle\xi_0^2\rangle$ is given, in the static approximation, by

$$\langle\xi_0^2\rangle_{st} = \frac{\int d\xi_0\,\xi_0^2 \exp[-\beta\widetilde{\Omega}(\xi_0)]}{\int d\xi_0 \exp[-\beta\widetilde{\Omega}(\xi_0)]}. \tag{19}$$

The form of $\Delta\chi$ as function of $\beta\Gamma$ is given in fig. 3, for $u = 10$. For comparison, we have also given the result for $U = \infty$, $\epsilon = -\frac{1}{2}$. We see how $\Delta\chi$ tends to be

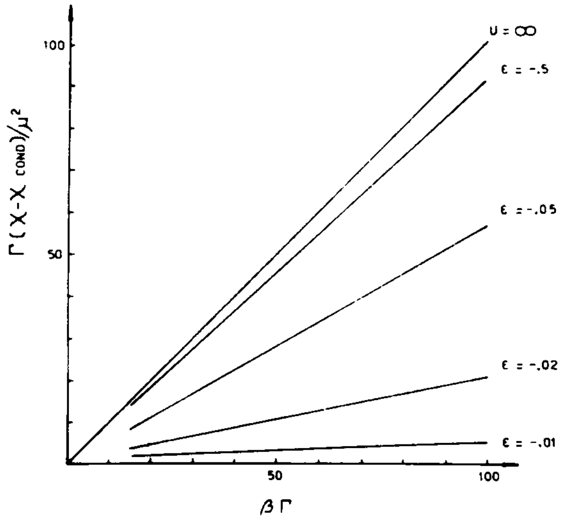

Fig. 3. Excess susceptibility $\Delta\chi$ as a function of $\beta\Gamma$, for $u = 10$, in the two field approach. The result for $u \to \infty$ in the symmetric case is shown as reference.

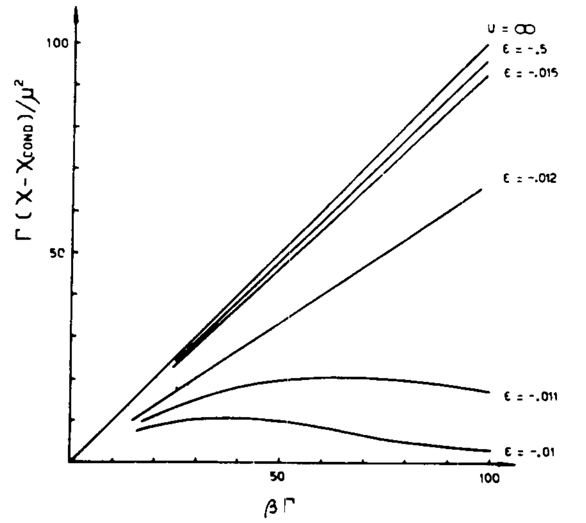

Fig. 5. Excess susceptibility $\Delta\chi$ as a function of $\beta\Gamma$, for $u = 10$, in the single field approach. The result for $u \to \infty$ in the symmetric case is shown as reference.

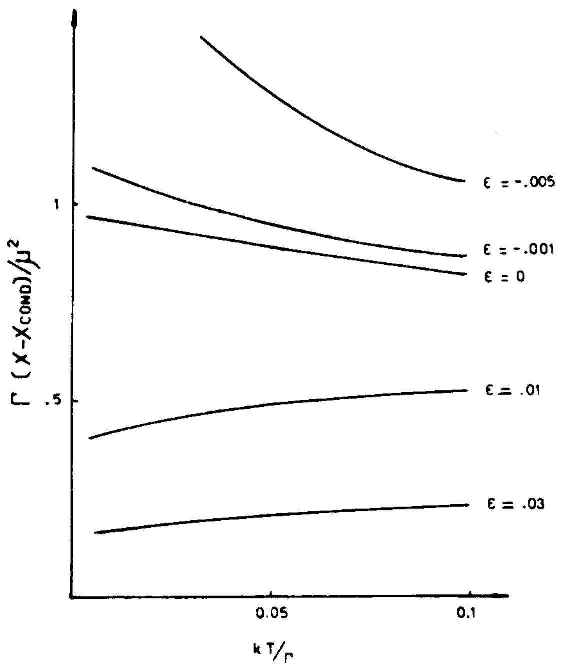

Fig. 4. Excess susceptibility $\Delta\chi$ as function of kT/Γ, for $u = 10$, in the two field approach. For $\epsilon > -1/10$ the susceptibility saturates as $T \to 0$.

temperature independent as the level approaches the Fermi energy.

In fig. 4 we plotted $\Delta\chi$ against T for different values of ϵ. We see that for $\epsilon > 0$, the susceptibility increases with T due to the increase in population of the impurity level as the temperature rises. In the one field approximation, $\Delta\chi$ gives a Curie law even when the level lies near the Fermi energy, and the demagnetization is not progressive but abrupt, as is shown in fig. 5. We see from fig. 4 how this is improved in the present case.

It is important to emphasize that the previous results are in complete agreement with the general trends, for the dependence of χ on the parameters U, Γ and E, as suggested by Wilson et al. [12] on the grounds of a renormalization group approach for the Anderson Model. These trends are: (i) for fixed T, U and Γ, χ decreases with increasing E (from $-U/2$); (ii) for fixed T, E and Γ, χ increases with increasing U; (iii) for fixed T, U and E, χ decreases with increasing Γ; (iv) for the symmetric case ($E = -U/2$), for fixed T and Γ, χ increases with increasing U, a result which is a consequence of (i) and (ii).

We feel that our conclusions are of significance to

Wohlleben's [13] qualitative discussion of a saturating static susceptibility induced by valence fluctuations as is found in metallic Cerium [14], in some of the rare earth monochalcogenides and related compound [15], in Sm B_6 [16], etc.

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References

[1] S.Q. Wang, W.E. Evenson and J.R. Schrieffer, Phys. Rev. Lett. 23 (1969) 92; J. Appl. Phys. 41 (1970) 1199.
J.R. Schrieffer, CAP School Lecture Note (1969) unpublished.

[2] D.R. Hamann, Phys. Rev. Lett. 23 (1969) 95, Phys. Rev. B2. (1970) 1376.
D.R. Hamann and J.R. Schrieffer, Magnetism, vol. 5, H. Suhl, ed. (Academic Press, New York, 1971).

[3] H. Keiter, Phys. Rev. B2 (1970) 3777.
D.J. Amit and H. Keiter, Preprint (1972).

[4] R.F. Hassing and D.M. Esterling, Phys. Rev. B7 (1973) 432.
G. Morandi, E. Galleani d'Agliano, F. Napoli and C.F. Ratto, Adv. Phys. 23 (1974) 867 and references cited therein.
B. Kjöllerström, Phys. Stat. Sol. (b) 43 (1971) 203, as indicated in the review of Morandi et al., used the extreme approximation in the η field, although that is not clearly stated in his paper.

[6] P.W. Anderson, Phys. Rev. 124 (1961) 43.

[7] R.L. Stratonovich, Dokl. Akad. Nauk. SSSR 115 (1975) 1097. (English transl.: Soviet Phys. Doklady 2 (1958) 416.
J. Hubbard, Phys. Rev. Lett. 3 (1959) 77.

[8] R.A. Bari, Phys. Rev. B5 (1972) 2736.

[9] A. López and C. Balseiro, Power Spectrum of Valence Fluctuations (to be published).

[10] B. Alascio, A. López and C.E.F. Olmedo, Phys. F3 k (1973) 1324.
H.S. Wio, B. Alascio and A. López, Solid St. Comm. 15 (1974) 1933.

[11] F. Meunier, S. Ortega, O. Peña, M. Roth and B. Coqblin, Solid St. Comm. 14 (1974) 1091.

[12] H.R. Krishna–Murthy, K.G. Wilson and J.W. Wilkins, Proc. Int. Conf. on Valence Instabilities and ..., (Rochester, N.Y., 1976) to be published.

[13] B.C. Sales and D.K. Wohlleben, Phys. Rev. Lett. 35 (1975) 1240 and references therein.

[14] M.R. Mc Pherson, G.E. Everett, D. Wohlleben and M.B. Maple, Phys. Rev. Lett. 26 (1971) 20.

[15] A. Jayaraman, P.D. Dernier and L.D. Longinotti, High Temp- High Preassures 7 (1975) 1 and references cited therein.

[16] J.C. Nickerson, R.B. White, K.N. Lee, R. Buchmann, T.H. Geballe and G.W. Hull, Phys. Rev. B3 (1974) 2030.