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Charge-density oscillations in intermediate-valence and Kondo systems

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Spatial variation of conduction-electron charge-density perturbation around 3*d* or 4*f* impurities in normal metals is investigated within the single-orbital Anderson model. Using the perturbation theory we calculate $\delta\rho_c(r,T)$ in various points of the parameter space. The Kondo region, the valence-fluctuating region, and the nearly-empty-orbital region are discussed. We also discuss the relevance of our results for the explanation of the experimentally observed features of charge-density oscillations in some dilute alloys.

I. INTRODUCTION

Experimental studies[1–18] of charge-density oscillations (CDO) around transition-metal or rare-earth impurities in normal-metal hosts have revealed two principal features.

(i) The amplitude of CDO in the vicinity of the impurity can be considerably reduced with respect to the values predicted by Friedel's asymptotic expression

$$\delta\rho_c(r) \to -\frac{\alpha}{2\pi^2 r^3}\cos(2k_F r+\phi) \ . \tag{1}$$

(ii) In Kondo (or "magnetic") alloys, CDO exhibit the same strong temperature dependence as the electric resistivity or thermoelectric power.[5,6]

Expression (1) was an early attempt to understand the phenomenon of CDO in dilute alloys, and has persisted ever since in the literature as a standard reference to compare the experimental and theoretical results with, as well as for its simplicity. It was obtained by the partial-wave analysis of scattering of free conduction electrons on the localized impurity potential, for $T=0$ and for large distances from the impurity.[19,20] The amplitude $\alpha \equiv |\alpha|$ and the phase ϕ are related to the conduction-electron scattering phase shifts $\eta_l(\varepsilon)$, evaluated at the Fermi energy ε_F, as

$$\alpha e^{i\phi} = \sum_{l=0}^{\infty}(-1)^l(2l+1)[\sin\eta_l(\varepsilon_F)]e^{i\eta_l(\varepsilon_F)} \ . \tag{2}$$

The phase shifts satisfy the Friedel sum rule,[21] i.e., the charge-neutrality condition

$$\sum_{l=0}^{\infty}(2l+1)\eta_l(\varepsilon_F)=\pi Z/2 \ , \tag{3}$$

where Z is the total screening charge (in units of e), equal to the excess charge of the impurity. In case of transition-metal or rare-earth impurities, the electronic properties are presumably dominated by the strong resonant scattering of conduction electrons on the unfilled d (or f) shell of the impurity, and within the context of the phase-shift analysis, the $l=2$ (or 3) phase shift dominates. If the effects of other phase shifts are neglected, the Friedel sum rule (3) reduces to $\eta_l(\varepsilon_F)=\pi Z/2(2l+1)$ and the amplitude and phase of expression (1) become $\alpha=(-1)^l(2l+1)[\sin\eta_l(\varepsilon_F)]$ and $\phi=\eta_l(\varepsilon_F)$, i.e., they are uniquely determined by the charge-neutrality condition alone.

Deviations of the experimental data from Eq. (1) indicate that (i) the energy dependence of phase shifts, neglected in Friedel's derivation, has to be taken into account, and (ii) rather than extrapolating the asymptotic expression down to the distances that are accessible to experiment, one should explicitly calculate the spatial dependence of CDO for all relevant distances. Also, one needs a finite-temperature theory to account for the strong temperature dependence of CDO.

To study the CDO around 3*d* or 4*f* impurities in normal metals, we assume that the essential electronic properties of such dilute alloys are sufficiently well described by the nondegenerate single-orbital Anderson model.[22] The Hamiltonian is defined as

$$H_A=\sum_{\mathbf{k},\sigma}\varepsilon_{\mathbf{k}}n_{\mathbf{k}\sigma}+\sum_{\mathbf{k},\sigma}(V_{\mathbf{k}d}c^{\dagger}_{\mathbf{k}\sigma}c_{d\sigma}+V_{d\mathbf{k}}c^{\dagger}_{d\sigma}c_{\mathbf{k}\sigma}) +\varepsilon_d\sum_{\sigma}n_{d\sigma}+Un_{d\uparrow}n_{d\downarrow} \ , \tag{4}$$

where all the symbols have the usual meaning. The index d is meant to denote a localized orbital of any kind, not necessarily an $l=2$ shell, and is used whenever the orbital quantum number l is irrelevant. The model assumes the dominance of a single resonant phase shift which, however, has an intricate energy and temperature dependence. Thus, the conduction-electron scattering matrix is simply related to the Green's function of localized electrons as

$$t^{\sigma}_{\mathbf{k}\mathbf{k}'}(z)=\sum_{m=-l}^{l} V_{\mathbf{k}m}G_{d\sigma}(z)V_{m\mathbf{k}'} \ . \tag{5}$$

Given the scattering matrix, one can calculate the conduction-electron charge-density (CD) perturbation due to the presence of the impurity, $\delta\rho_c$, as a function of distance from the impurity and temperature.

At $T=0$ and for large distances, the CD perturbation turns out to be given by

$$\delta\rho_c(r,T=0)=-\frac{(-1)^l(2l+1)\sin(\pi n_d/2)}{2\pi^2 r^3} \times\cos(2k_F r+\pi n_d/2)+O(r^{-4}) \ , \tag{6}$$

where n_d is the average number of localized electrons at $T=0$. The leading ($\propto r^{-3}$) term in (6) neglects the energy dependence of the conduction-electron scattering matrix, i.e., it is obtained with $G_{d\sigma}(\varepsilon\pm i0^+)=G_{d\sigma}(\pm i0^+)$. It coincides with Friedel's asymptotic expression (1) with $\alpha=(-1)^l(2l+1)\sin(\pi n_d/2)$ and $\phi=\pi n_d/2$, that is, with only a single phase shift $\eta_l(\varepsilon_F)$ different from zero (the one corresponding to the symmetry of the localized orbital) and equal to $\pi n_d/2$. Here $n_d=Z/(2l+1)$, since in the Anderson model with the infinite and constant host conduction band and constant $V_{\mathbf{k}d}$ the total screening of the excess impurity charge is done by the localized electrons alone. [That is, $\delta\rho_c(\mathbf{r},T)$ is, strictly speaking, *not* the *screening* charge.]

The higher-order ($\propto r^{-4}$, etc.) terms in (6) originate from the energy dependence of both the scattering matrix and the unperturbed Green's function of conduction electrons. For most values of the model parameters, the energy dependence of the former gives the dominant contribution to the r^{-4} term.

Anyhow, the leading term of (6) becomes dominant for large enough values of r. In the Hartree-Fock (HF) approximation one obtains[23] that "large enough" means

$$k_F r \gg k_F R_{\mathrm{HF}}=(\varepsilon_F/\Delta)\sin(\pi n_d/2) \ . \tag{7}$$

Since $\varepsilon_F/\Delta\simeq 10$ for aluminum- and copper-based alloys,[24] it would be tempting to conclude that Friedel's asymptotic expression (1), which altogether neglects the energy dependence of the conduction-electron scattering matrix, is valid everywhere except at the first few neighboring shells around the impurity. This conclusion, however, is contradicted by the experimental data, which indicate that the scattering matrix must be a rapidly varying function of energy. Thus, the energy dependence of $t^{\sigma}_{\mathbf{k}\mathbf{k}'}$ is not to be neglected even for distances much larger than those predicted by the HF criterion (7). Furthermore, if one does include the energy dependence, the one offered by the HF approximation is insufficient to account for the observed effects [even if no further approximations are introduced in the calculation of $\delta\rho_c(r)$]. Namely, even if most of the experimental results on the so-called "nonmagnetic" alloys (like $\underline{\mathrm{Al}}$Sc)[10] could be explained within the one-electron approximation, the "anomalous" behavior of "magnetic" alloys (like $\underline{\mathrm{Al}}$Cr, $\underline{\mathrm{Al}}$Mn, or $\underline{\mathrm{Al}}$Fe)[11,12] clearly defies such a simple theory.

This is even more so for the temperature dependence of CDO. Just as in the case of thermodynamic and transport quantities, the HF approximation here also fails to reproduce the strong temperature dependence observed experimentally.[5,6]

To include the many-body (MB) effects in the conduction-electron scattering matrix, we calculate the localized-electron Green's function using the finite-temperature perturbation theory, developed first by Yosida and Yamada[25–28] for the symmetric Anderson model ($\varepsilon_d=-U/2$) and extended so as to allow the discussion of all the parameter space.[29–31] In such an approach, the mean-field part of the problem is solved first and the effect of fluctuations due to the local Coulomb correlation is treated as a perturbation. The expansion parameter is $u=U/\pi\Delta$, where $\Delta=\pi\langle|V_{\mathbf{k}d}|^2\rangle\rho^{(0)}_{c\sigma}(\varepsilon_F)$ is the half-width (at half maximum) of the Lorentzian-shaped local-electron spectral density for $U=0$. Here, rather than characterizing the system by the parameters u and ε_d/Δ, as is usually the case, we find it convenient to define the parameter space by u and the average number of localized electrons $n_d=\langle\langle n_{d\uparrow}\rangle\rangle+\langle\langle n_{d\downarrow}\rangle\rangle$ at $T=0$. It is well known[32,33] that the properties of the model depend sensitively on the values of u and n_d. For $n_d\simeq 1$ and $u\gg 1$ the Kondo effect is obtained, for n_d between 0.7 and 0.5 and $u\gg 1$ valence fluctuations are observed, while for $n_d\ll 1$ and arbitrary u or $u\ll 1$ and arbitrary n_d a simple resonant scattering of conduction electrons appears on the impurity d or f shell.

Using a finite-order perturbation theory to discuss the strong-correlation features of the Anderson model deserves a word of justification. The method, described in Refs. 33–35, has proven to be quantitatively correct even for $u\simeq 2.5$ as regards the thermodynamic and transport properties of the model. That is, the comparison of our finite-order perturbative results with those of the Bethe-ansatz method[36–40] for the physical quantities that can be obtained by both methods has shown good agreement not only for $u<1$, but also for $u>1$. On the other hand, the Anderson model has the remarkable property that the *smooth* crossover from the weak-correlation ($u\to 0$) to the strong-correlation regime ($u\to\infty$) takes place for $1\lesssim u\lesssim 2$. The low-order perturbative results are therefore able to describe correctly the transition to the strong-correlation regime, as well as to give a rather accurate account of the "lower edge" of the latter. The results obtained for $u=2.5$ reveal all the strong-correlation features, which remain qualitatively unchanged (and are only enhanced) with further increase of u. Thus, the low-order perturbation theory allows the discussion of those parts of the parameter space where the Kondo effect or valence fluctuations are observed.

Furthermore, while the Bethe-ansatz method[36–40] gives only those bulk properties of the system which depend on the electron states in the vicinity of the Fermi level,[40] the perturbation theory provides the single-particle Green's function at arbitrary energy, which allows the calculation of local properties, such as the spatial distribution of the spin and charge density around an impurity. The study of local properties requires the information about the complete spectrum of single-particle excitations in the system, not just those close to the Fermi level.

We have no direct quantitative proof that our perturbative method works equally well for the energy-dependent quantities as it does for thermodynamical averages. Our confidence is based on the physically reasonable results for the spectral density of local single-particle excitations for u as large as 2.5 and the qualitative comparison of these results with the analytic ones obtained for $u=\infty\,(V_{\mathbf{k}d}=0)$.[34,35]

One should mention here that the numerical renormalization-group method[41] has recently also been generalized so as to enable the calculation of finite-energy excitation properties for the Anderson model, in particular, the spectral density of local single-particle excitations.[42] These results could be used as an input to evaluate the spin and charge density distribution along the same lines as we do in this paper.

Local properties of an Anderson impurity and the surrounding conduction electrons have also been calculated by other methods, without direct reference to the finite-energy spectral density,[43,44] but none of these works was specifically concerned with the charge density. Chen, Jayaprakash, and Krishna-Murthy[43] applied the perturbative, thermodynamic scaling theory to the spin-$\frac{1}{2}$ Kondo model to study the zero-frequency spin-density response function related to the extra Knight shift for host nuclei. The method uses a combination of perturbative scaling that extracts the spatial dependence and nonperturbative methods such as the renormalization-group technique to calculate local correlation functions and extract the temperature dependence. Gubernatis, Hirsch, and Scalapino[44] calculated the spatial and temperature dependence of the correlations between the spin and charge at the impurity and those in the conduction states, within the symmetric single-impurity Anderson model and using a quantum Monte Carlo procedure. Their results for the charge correlations exhibit the same general trends as our present results for the charge-density perturbation: suppression of oscillations with increasing Coulomb interaction and temperature. However, a more detailed comparison is not possible since the physical quantities in question are not the same.

While it is true that those correlation functions which depend solely on the low-energy excitations of the system exhibit the universal behavior for some values of the model parameters ($n_d \simeq 1$ and $u \gg 1$), the situation regarding the local properties is more complicated. The single-particle d-electron Green's function, which determines the charge- and spin-density oscillations, is characterized by two distinct energy scales: the low-energy scale $k_B T_K$ and the high-energy scale Δ. The local properties depending on the total energy spectrum are not, in general, expected to exhibit the universal features.

In this paper we show that the correctly evaluated CDO exhibit the experimentally observed features. The energy dependence of the scattering matrix, resulting from the self-energy corrections caused by local Coulomb interactions, accounts for both the preasymptotic reduction of the amplitude of CDO and the strong temperature effects. In Sec. II we derive the general expression for the conduction-electron CD perturbation in the Anderson model. In Sec. III we obtain the analytic expression for the low-temperature $\delta\rho_c(r,T)$ at large distances from the impurity. We find out that the corrections to Friedel's asymptotic expression become negligible only for $r \gg R$, where R is larger by a factor of $\tilde{\gamma}$ than the mean-field estimate R_{HF}, defined by Eq. (7). These results also indicate that the behavior of CDO can be predominantly determined by the low-energy scale $k_B T_K$ for $r \sim R$, which we term the "preasymptotic region," but *not* in the asymptotic region proper, as defined above. For small distances, $r \ll R$, all energies contribute to $\delta\rho_c(r,T)$, and the high-energy scale Δ can dominate only if $\Delta/k_B T_K \gg 1$. Also, for small distances, the (single-particle) effects of the band structure of the host and its hybridization with the impurity orbital can be comparable to or even stronger than the MB self-energy corrections.

In Sec. IV we present numerical results for $\delta\rho_c(r,T)$ for small and preasymptotic distances and for arbitrary temperature, obtained for $l=2$ (d orbital) and with the scattering matrix evaluated by perturbation theory in various relevant parts of the parameter space. We discuss the influence of temperature, asymmetry, and Coulomb correlation on CDO. Section V contains a brief review of the experimental methods used to investigate CDO in dilute alloys and the discussion of some problems pertaining to the interpretation of experimental data and their linkage with theoretical results. Conclusions are summarized in Sec. VI.

II. CALCULATIONS

The change of the conduction-electron charge density due to the presence of the impurity is given by

$$\delta\rho_c(\mathbf{r},T) = \mp\frac{2}{\pi\mathcal{V}}\mathrm{Im}\int_{-\infty}^{\infty} d\varepsilon\, f(\varepsilon/k_B T) \times \sum_{\mathbf{k},\mathbf{k}'} \psi_{\mathbf{k}}(\mathbf{r})\psi^{*}_{\mathbf{k}'}(\mathbf{r})\,\delta G^{\sigma}_{\mathbf{k}\mathbf{k}'}(\varepsilon \pm i0^{+}) , \tag{8}$$

where

$$\delta G^{\sigma}_{\mathbf{k}\mathbf{k}'}(z) = G^{\sigma}_{\mathbf{k}\mathbf{k}'}(z) - G^{\sigma 0}_{\mathbf{k}\mathbf{k}'}(z) ,$$

$$G^{\sigma 0}_{\mathbf{k}\mathbf{k}'}(z) = \delta_{\mathbf{k}\mathbf{k}'}(z-\varepsilon_{\mathbf{k}})^{-1} ,$$

and $\varepsilon_{\mathbf{k}}$ and $\psi_{\mathbf{k}}(\mathbf{r})$ are the energy eigenvalues and eigenfunctions of the electrons in the pure-host conduction band. In the Anderson model the change of the conduction-electron Green's function is given by

$$\begin{aligned}\delta G^{\sigma}_{\mathbf{k}\mathbf{k}'}(z) &= G^{\sigma 0}_{\mathbf{k}\mathbf{k}}(z)\, t^{\sigma}_{\mathbf{k}\mathbf{k}'}(z)\, G^{\sigma 0}_{\mathbf{k}'\mathbf{k}'}(z) \\ &= \left[\sum_{m=-l}^{l} V_{\mathbf{k}m} V_{m\mathbf{k}'}\right] G^{\sigma 0}_{\mathbf{k}\mathbf{k}}(z)\, G^{\sigma 0}_{\mathbf{k}'\mathbf{k}'}(z)\, G_{d\sigma}(z) ,\end{aligned} \tag{9}$$

and the localized-electron Green's function $G_{d\sigma}$ can be written as[33]

$$\begin{aligned}G_{d\sigma}(i\omega_n) = [\, & i\omega_n - (\varepsilon_d + \langle\langle n_{d\sigma}\rangle\rangle U) \\ & + i\Delta\omega_n/|\omega_n| - \tilde{\Sigma}_{d\sigma}(i\omega_n)]^{-1} ,\end{aligned} \tag{10}$$

where $\tilde{\Sigma}_{d\sigma}$ is the self-energy one has to calculate. Assuming the spherically symmetric impurity potential and the simple plane-wave dispersion in the pure-host conduction band,

$$\psi_{\mathbf{k}}(\mathbf{r})=\mathcal{V}^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}} , \tag{11}$$

one has

$$V_{\mathbf{k}m}=N^{-1/2}V_l(k)Y_l^m(\hat{k}) . \tag{12}$$

Furthermore, we neglect the $|\mathbf{k}|$ dependence of $V_{\mathbf{k}m}$ by replacing $V_l(k)$ with its RMS average over k. These approximations result in

$$\delta G^{\sigma}_{\mathbf{kk}'}(z)=\frac{2l+1}{\pi}\frac{\Delta}{\rho^{(0)}_{c\sigma}}\frac{P_l(\hat{k}\cdot\hat{k}')}{(z-\varepsilon_{\mathbf{k}})(z-\varepsilon_{\mathbf{k}'})}G_{d\sigma}(z) , \tag{13}$$

where P_l is the Legendre polynomial. Inserting expressions (11) and (13) into (8) and evaluating the angular part of the $\mathbf{k}$ and $\mathbf{k}'$ integration, one can write the expression for $\delta\rho_c$ as[23,45]

$$\delta\rho_c(r,T)=-\frac{2l+1}{2\pi^2}\frac{\Delta}{\varepsilon_F}\frac{k_F^3}{(k_Fr)^2}\times\mathrm{Im}\int_{-\infty}^{\infty}d\varepsilon\, f(\varepsilon/k_BT)g_l^2(\varepsilon,r)G_{d\sigma}(\varepsilon+i0^+) . \tag{14}$$

For a given angular momentum l, the function $g_l(\varepsilon,r)$ is defined as

$$g_l(\varepsilon,r)=\frac{2}{\pi}\int_0^{\infty}\frac{x^2j_l(x)dx}{x^2-(kr)^2-i0^+} , \tag{15}$$

where $j_l(x)$ is the spherical Bessel function and

$$k=k(\varepsilon)\equiv k_F(1+\varepsilon/\varepsilon_F)^{1/2} . \tag{16}$$

Equations (14), (15), and (10), together with the exact expression for $\tilde{\Sigma}_{d\sigma}(\varepsilon+i0^+)$, provide the formal solution for $\delta\rho_c(r,T)$ within the Anderson model. We evaluate the self-energy of localized electrons using the perturbation technique described in detail in Refs. 34 and 35. Once $\tilde{\Sigma}_{d\sigma}(\varepsilon+i0^+)$ is obtained, the CD perturbation at a distance r from the impurity and temperature T is calculated by numerical integration of Eq. (14).

There are a few points to be noted.

(i) The energy is measured from the Fermi level, so that the bottom of the host conduction band is at $-\varepsilon_F$.

(ii) $k(\varepsilon)$ is real for $\varepsilon>-\varepsilon_F$ and becomes imaginary if $\varepsilon<-\varepsilon_F$. Consequently, $g_l(\varepsilon,r)$ changes its functional form at $\varepsilon=-\varepsilon_F$.

(iii) The integration over ε in (14) is *not* restricted to the conduction band (as it derives from the summation over Fermi frequencies ω_n and has nothing to do with $\varepsilon_{\mathbf{k}}$'s). The cutoff at high energies is provided by the Fermi function $f(\varepsilon/k_BT)$, and that below $-\varepsilon_F$ by the function $g_l(\varepsilon,r)$.

(iv) The specific form of $g_l(\varepsilon,r)$, which enters the calculation of $\delta\rho_c(r,T)$, depends rather strongly on the assumptions regarding the hybridization matrix element $V_{\mathbf{k}m}$ and the unperturbed conduction-band Green's function $G^{\sigma 0}_{\mathbf{kk}'}$.

For even l the function $g_l(\varepsilon,r)$ is calculated by contour integration as

$$g_l(\varepsilon,r)=e^{i(kr-l\pi/2)}\sum_{m=0}^{l}\frac{i^m(l+m)!}{(2m)!!!(l-m)!}(kr)^{-m}+i^l\sum_{m=0}^{l-2}\frac{(-1)^m(l+m+2)!}{(2m+4)!!!(l-m-2)!}\times\sum_{n=0}^{[m/2]}\frac{(-1)^n}{(m-2n)!}(kr)^{-2(n+1)} . \tag{17}$$

For $|k(\varepsilon)r|\gg 1$, i.e., if $|1+\varepsilon/\varepsilon_F|\gg(k_Fr)^{-2}$, the leading term is given by

$$g_l(\varepsilon,r)\simeq\begin{cases} e^{i(kr-l\pi/2)} & \text{if } \varepsilon>-\varepsilon_F \\ \left[i^l\sum_{m=0}^{l-2}\frac{(-1)^m(l+m+2)!}{m!(2m+4)!!!(l-m-2)!}\right](kr)^{-2} & \text{if } \varepsilon<-\varepsilon_F . \end{cases} \tag{18}$$

Thus, if (and only if !) $k_Fr\gg 1$, $g_l(\varepsilon,r)$ can be replaced by its asymptotic form (18) for almost all energies, with the exception of the narrow interval around the bottom of the conduction band. If, however, k_Fr is not large enough, this substitution means using a wrong integrand in Eq. (14) in a large part of the domain of integration, which leads to a completely wrong result for $\delta\rho_c(r)$.

As an example, in Fig. 1 we compare $\delta\rho_c(r,T=0)$ for $u=2.5$ and $n_d=1$ evaluated with the exact function

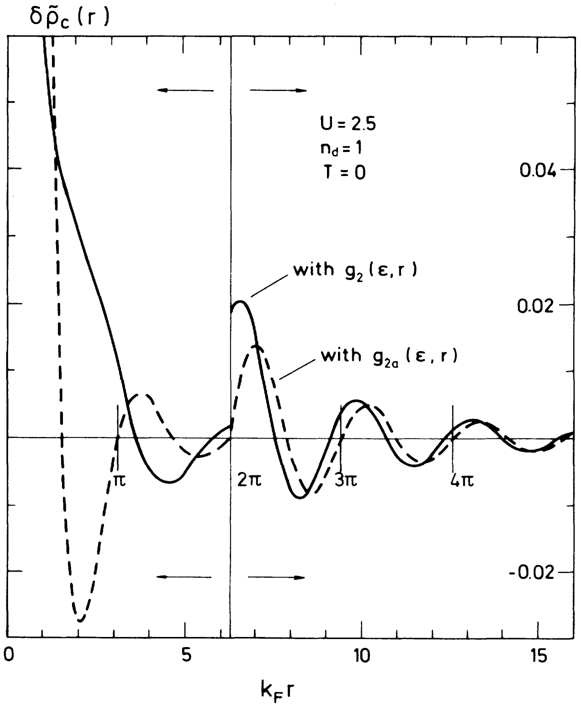

FIG. 1. Comparison of $\delta\tilde{\rho}_c(r,T=0)\equiv[k_F^3(2l+1)\Delta/2\pi^2\varepsilon_F]^{-1}\delta\rho_c(r,T=0)$ for $u=2.5$ and $n_d=1$ calculated with the exact function $g_2(\varepsilon,r)$ (solid line) and with its asymptotic form $g_{2a}(\varepsilon,r)=-e^{ik(\varepsilon)r}$ (dashed line).

$$g_2(\varepsilon,r)=(kr)^{-2}\{[3-3ikr-(kr)^2]e^{ikr}-3\} \tag{19}$$

(solid line) and with its asymptotic form $g_{2a}(\varepsilon,r)=-e^{ikr}$ (dashed line). One can see that the results obtained with g_{2a} deviate appreciably from those evaluated with g_2 for $k_F r$ as large as $\sim 4\pi$. This is no wonder since, as we show in Sec. III, the replacement of g_l with g_{la} under the integral (14) for $\delta\rho_c(r)$ becomes justified only for $k_F r \gg l(l+1)$, that is, for $k_F r \gg 6$ in the $l=2$ case.

This also illustrates the fact that the results for $\delta\rho_c(r)$ are rather sensitive to the specific form of $g_l(\varepsilon,r)$, which, for its part, depends rather strongly on the single-particle model parameters $V_{\mathbf{k}m}$ and $\varepsilon_{\mathbf{k}}$.

III. ASYMPTOTIC REGION

For $T=0$ the Fermi integral in Eq. (14) for the CD perturbation reduces to

$$\int_{-\infty}^{0} g_l^2(\varepsilon,r)G_{d\sigma}(\varepsilon+i0^+)d\varepsilon \ . \tag{20}$$

In order to obtain the asymptotic expression for $\delta\rho_c(r,T=0)$ in the limit of large $k_F r$, we insert the expansion

$$g_l^2(\varepsilon,r)=(-1)^l e^{i2k(\varepsilon)r}\left[1+i\frac{l(l+1)}{k(\varepsilon)r}+O(r^{-2})\right] \tag{21}$$

into the integral (20) and make use of the formula

$$\int_{-\infty}^{0} e^{i2k(\varepsilon)r}F(\varepsilon,r)d\varepsilon=-\left[\frac{i\varepsilon_F}{k_F r}\right]e^{i2k_F r}\sum_{n=0}^{\infty}\left[\frac{i\varepsilon_F}{k_F r}\right]^n\left\{\left[\left[1+\frac{\varepsilon}{\varepsilon_F}\right]^{1/2}\frac{\partial}{\partial\varepsilon}\right]^n\left[\left[1+\frac{\varepsilon}{\varepsilon_F}\right]^{1/2}F(\varepsilon,r)\right]\right\}_{\varepsilon=0} , \tag{22}$$

obtained by repeated partial integration, with

$$F(\varepsilon,r)=\left[1+i\frac{l(l+1)}{k(\varepsilon)r}+\cdots\right]G_{d\sigma}(\varepsilon+i0^+) \ .$$

The integral (20) can thus be expanded as

$$(-1)^{l+1}\left[\frac{\varepsilon_F}{k_F r}\right]e^{i2k_F r}\left[\left[i-\frac{l(l+1)+\frac{1}{2}}{k_F r}\right]G_{d\sigma}(i0^+) + \left[\frac{\varepsilon_F\tilde{\gamma}}{k_F r}\right]G_{d\sigma}^2(i0^+)+O(r^{-2})\right] , \tag{23}$$

where

$$\tilde{\gamma}=1-[\partial\tilde{\Sigma}_{d\sigma}(\varepsilon)/\partial\varepsilon]_{\varepsilon=T=0} \ . \tag{24}$$

At $T=0$ the value of localized-electron Green's function at the Fermi energy is determined solely by the charge-neutrality condition, viz.,

$$G_{d\sigma}(i0^+)=-\Delta^{-1}\sin(\pi n_d/2)\exp(i\pi n_d/2) \ , \tag{25}$$

where n_d is the solution of the transcendental equation[46,47,33]

$$\cot(\pi n_d/2)=(\varepsilon_d/\Delta)+(\pi n_d/2)u+\tilde{\Sigma}_{d\sigma}(i0^+)/\Delta \ . \tag{26}$$

Inserting (25) into (23) and taking the imaginary part of the resulting expression, one finally obtains

$$\begin{aligned}\delta\rho_c(r,T=0)=-\frac{(-1)^l(2l+1)\sin(\pi n_d/2)}{2\pi^2 r^3}&(\cos(2k_F r+\pi n_d/2)\\&-(k_F r)^{-1}\{(\varepsilon_F/\Delta)\tilde{\gamma}\sin(\pi n_d/2)\sin(2k_F r+\pi n_d)\\&+[l(l+1)+\tfrac{1}{2}]\sin(2k_F r+\pi n_d/2)\}+O(r^{-2})) \ .\end{aligned} \tag{27}$$

The leading term of this large-r expansion is recognized as Friedel's asymptotic expression, as it should be. The first $(k_F r)^{-4}$ term originates in the energy dependence (first derivative at ε_F) of $G_{d\sigma}(\varepsilon+i0^+)$. It is present already in the HF approximation, but $\tilde{\gamma}$ adds the self-energy (correlation) effects. The second $(k_F r)^{-4}$ term, proportional to $l(l+1)$, comes from the "nonasymptoticity" of $g_l(\varepsilon,r)$, i.e., from its first-order deviation from $\exp[i(kr-l\pi/2)]$. Finally, the third $(k_F r)^{-4}$ term, proportional to $\frac{1}{2}$, comes from the energy dependence of k in the asymptotic expression for $g_l(\varepsilon,r)$. It is obtained even if one neglects both the energy dependence of $G_{d\sigma}(\varepsilon+i0^+)$ and the "nonasymptoticity" of $g_l(\varepsilon,r)$, but has usually been omitted.

Terms of still higher order in $(k_F r)^{-1}$, which involve higher-order derivatives of the Green's function, cannot be written or interpreted so neatly. They are, however, of no importance here, since the expansion (27) is an *asymptotic* one and, consequently, cannot describe $\delta\rho_c(r)$ correctly at small distances, no matter how many terms are taken into account. The first correction to the leading term, given in expression (27), suffices to define the asymptotic region.

One should also mention that $\delta\rho_c(r)$ comprises the aperiodic terms as well, originating from the part of $g_l(\varepsilon,r)$ that is not proportional to $\exp(ikr)$ [the second line of Eq. (17)], but those terms are of the order of $(k_F r)^{-5}$ and higher, which is neglected in expression (27). This contribution shows up, however, at small distances from the impurity, disturbing the oscillatory nature of CD perturbation, as shown in Sec. IV.

It is obvious from expression (27) that the first-order corrections to the asymptotic term become negligible for

$$r \gg r_a = \max\{R, r_l + \tfrac{1}{2}k_F^{-1}\} , \tag{28}$$

where the radii R and r_l are defined as

$$k_F R = (\varepsilon_F/\Delta)\tilde{\gamma}\sin(\pi n_d/2) , \tag{29}$$

$$k_F r_l = l(l+1) , \tag{30}$$

while the "nonasymptoticity" of $g_l(\varepsilon,r)$ can be neglected for

$$r \gg r_l . \tag{31}$$

The first of these two criteria defines the asymptotic region of $\delta\rho_c(r,T=0)$, where Friedel's expression is a good approximation, while the second one defines the distances for which the asymptotic form of $g_l(\varepsilon,r)$ becomes justified under the integral (20). For most of the physically interesting cases this is not one and the same.

Which of the two radii, R and r_l, is larger for reasonable values of model parameters? Since $\tilde{\gamma} \geq 1$ and $\varepsilon_F/\Delta \gg 1$, and if l is not too large ($l=2,3$), one has $R > r_l$ for most values of n_d except for $n_d \ll 1$ and $2-n_d \ll 1$ (almost empty and almost full localized orbital). Thus, apart from these two extreme cases, the asymptotic radius r_a is equal to R, and the $(k_F r)^{-4}$ term originating from the energy dependence of the Green's function is the dominant correction to $\delta\rho_c^F(r)$.

The inclusion of MB effects caused by the local Coulomb correlation pushes the onset of the asymptotic behavior of $\delta\rho_c(r,T=0)$ to distances larger by the factor of $\tilde{\gamma}$ than those predicted by the HF approximation [Eq. (7)]. That is, $R/R_{\mathrm{HF}} = \tilde{\gamma} \geq 1$, where $\tilde{\gamma} \equiv \tilde{\gamma}(u,n_d)$, defined by Eq. (24), is the well-known MB enhancement factor which reflects the Fermi-liquid properties of the Anderson model at low energies and/or temperatures. As a function of n_d, $\tilde{\gamma}$ has the maximum for $n_d=1$, i.e., in the case of electron-hole symmetry. As a function of u, $\tilde{\gamma}$ increases monotonically with the increase of u. This rise is the quickest for $n_d=1$, where it becomes exponential for $u \gtrsim 1$. As an example, in the symmetric case one has $R/R_{\mathrm{HF}} = 2.506$, 4.181, and 7.166 for $u=1.5$, 2, and 2.5, respectively, which shows that the HF approximation can underestimate the asymptotic radius by quite a large factor, depending on the region of the parameter space.

One should note that the asymptotic expression for $\delta\rho_c(r)$ itself bears no trace of the local Coulomb correlation. It is the *deviation* from the asymptotic expression that is proportional to $\tilde{\gamma}$, and therefore the local Coulomb correlation creeps in $\delta\rho_c(r,T=0)$ as r is *diminished* towards R. Its influence on the CD perturbation reaches its full strength for distances $r \lesssim R$, but in that region it cannot be expressed by a single parameter like $\tilde{\gamma}$.

In other words, $\tilde{\gamma}$ sets the low-energy scale $\tilde{\Delta} = \Delta/\tilde{\gamma}$, which shows up in those properties of the system that depend solely on the low-energy local single-particle excitations. As a *functional* of $G_{d\sigma}(\varepsilon+i0^+)$, $\delta\rho_c(r,T=0)$ does not single out a particular energy region unless $r \to \infty$, in which case it averages out all energies except those in the immediate vicinity of the Fermi level. Since Friedel's expression depends only on the value of $G_{d\sigma}$ exactly at the Fermi level, it does not contain any local energy parameter at all. The first one that appears in $\delta\rho_c(r,T=0)$ as r is diminished towards R is $\tilde{\Delta}$, featured in the amplitude of the first-order correction to $\delta\rho_c^F(r)$ in the form of the ratio $\varepsilon_F/\tilde{\Delta}$. As r is diminished further, below R, all energies become important, and one cannot say that the low-energy scale $\tilde{\Delta}$ simply gives way to the high-energy scale Δ, unless $\Delta/\tilde{\Delta} = \tilde{\gamma} \gg 1$.

In the case of electron-hole symmetry ($n_d=1$), the expansion (27) simplifies to

$$\begin{aligned}\delta\rho_c(r,0) = {} & [(-1)^l(2l+1)/(2\pi^2 r^3)] \\ & \times\{[1-(R/r)+\cdots]\sin(2k_F r) \\ & \quad +[(r_l+\tfrac{1}{2}k_F^{-1})/r+\cdots]\cos(2k_F r)\} ,\end{aligned} \tag{27$'$}$$

with $k_F R = (\varepsilon_F/\Delta)\tilde{\gamma}(u, n_d=1)$. This expression clearly shows the preasymptotic *reduction* of the CDO amplitude whenever $R > r_l$.

Fermi-liquid properties can also be expected to show up in the temperature dependence of $\delta\rho_c(r,T)$ as $T \to 0$. The low-temperature T^2 correction of $\delta\rho_c$ comprises two terms:

$$\begin{aligned}\delta\rho_c(r,T)-\delta\rho_c(r,0) = -\frac{2l+1}{2\pi^2}\left[\frac{\Delta}{\varepsilon_F}\right]\frac{k_F^3}{(k_F r)^2}\left[\frac{\pi k_B T}{\Delta}\right]^2 \mathrm{Im}\Bigg[& \int_{-\infty}^{0} g_l^2(\varepsilon,r)G_{d\sigma}^2(\varepsilon+i0^+,0)[\tfrac{1}{2}U\mathcal{N}+\mathcal{S}(\varepsilon)]\,d\varepsilon \\ & +\tfrac{1}{6}\Delta^2\frac{\partial[g_l^2(\varepsilon,r)G_{d\sigma}(\varepsilon+i0^+,0)]}{\partial\varepsilon}\Bigg|_{\varepsilon=0}\Bigg]+O(T^4) .\end{aligned} \tag{32}$$

The first term is due to the *temperature* dependence of the Green's function,

$$G_{d\sigma}(\varepsilon+i0^+,T)-G_{d\sigma}(\varepsilon+i0^+,0)=G_{d\sigma}^2(\varepsilon+i0^+,0)[\tfrac{1}{2}U\mathcal{N}+\mathcal{S}(\varepsilon)](\pi k_B T/\Delta)^2+O(T^4) , \tag{33}$$

where $\mathcal{N}$ and $\mathcal{S}(\varepsilon)$ are defined by

$$n_d(T)=n_d+(\pi k_B T/\Delta)^2\mathcal{N}+O(T^4)\ , \tag{34}$$

$$\tilde{\Sigma}_{d\sigma}(\varepsilon+i0^+,T)=\tilde{\Sigma}_{d\sigma}(\varepsilon+i0^+,0)+(\pi k_B T/\Delta)^2\mathcal{S}(\varepsilon)+O(T^4)\ , \tag{35}$$

while the second one originates from the Sommerfeld expansion of the Fermi integral in (14), i.e., from the *energy* dependence of $g_l(\varepsilon,r)$ and $G_{d\sigma}(\varepsilon+i0^+,0)$ in the vicinity of the Fermi level. In the limit of large $k_F r$, the integral in (32) can be expanded in powers of $(k_F r)^{-1}$ along the same lines [Eqs. (21)–(25)] as has been done for $\delta\rho_c(r,0)$, with the result

$$\begin{aligned}\mathcal{T}_1\equiv{}&\frac{(-1)^l(2l+1)\sin(\pi n_d/2)}{2\pi^2 r^3}\left[\left(\frac{\pi k_B T}{\Delta}\right)^2\sin(\pi n_d/2)\right]\\&\times\frac{1}{\Delta}\{[\tfrac{1}{2}U\mathcal{N}+\mathrm{Re}\mathcal{S}(0)]\cos(2k_F r+\pi n_d)-\mathrm{Im}\mathcal{S}(0)\sin(2k_F r+\pi n_d)+O(R/r)\}\ .\end{aligned} \tag{36}$$

For the derivative term of (32) we obtain

$$\begin{aligned}\mathcal{T}_2\equiv{}&\frac{(-1)^l(2l+1)\sin(\pi n_d/2)}{2\pi^2 r^3}\left[\frac{1}{6}\left(\frac{\pi k_B T}{\varepsilon_F}\right)^2(k_F r)^2\right]\\&\times\{\cos(2k_F r+\pi n_d/2)+(R/r)[\sin(2k_F r+\pi n_d)-(r_l/R)\sin(2k_F r+\pi n_d/2)]+O[(R/r)^2]\}\ .\end{aligned} \tag{37}$$

The comparison of these two contributions shows that the ratio of their leading terms is

$$\mathcal{T}_1/\mathcal{T}_2\sim[6(\varepsilon_F/\Delta)^2\sin(\pi n_d/2)|\tfrac{1}{2}U\mathcal{N}+\mathcal{S}(0)|\Delta^{-1}]/(k_F r)^2\ , \tag{38}$$

so that one can expect that $\mathcal{T}_1 \ll \mathcal{T}_2$ for large $k_F r$.

In the symmetric case, $n_d=1$, we know $\mathcal{N}$ and $\mathcal{S}(0)$ exactly,[26–28]

$$\mathcal{N}=0,\quad \mathcal{S}(0)=-i\tfrac{1}{2}\Delta\tilde{\chi}^2_{\mathrm{odd}}\ , \tag{39}$$

and the low-temperature T^2 correction assumes a more transparent form

$$\begin{aligned}\delta\rho_c(r,T)-\delta\rho_c(r,0)&=\mathcal{T}_1+\mathcal{T}_2\\&=-\frac{(-1)^l(2l+1)}{2\pi^2 r^3}\sin(2k_F r)\left[\tfrac{1}{6}(k_F r)^2\left(\frac{\pi k_B T}{\varepsilon_F}\right)^2\right]\\&\qquad\times\{1+(R/r)[1+(r_l/R)\cot(2k_F r)]+\cdots+3(R/r)^2(\tilde{\chi}_{\mathrm{odd}}/\tilde{\gamma})^2+\cdots\}\ ,\end{aligned} \tag{40}$$

where the last term represents the contribution of $\mathcal{T}_1$. The ratio of the two contributions for $r \gg R$ becomes simply

$$\mathcal{T}_1/\mathcal{T}_2\sim 3(\tilde{\chi}_{\mathrm{odd}}/\tilde{\gamma})^2(R/r)^2\ . \tag{41}$$

It is well known[26] that in the symmetric case

$$\frac{\tilde{\chi}_{\mathrm{odd}}}{\tilde{\gamma}}\longrightarrow\begin{cases}0 \text{ as } u\to 0\\ 1 \text{ as } u\to\infty\end{cases} \tag{42}$$

and that the large-u limit of 1 is approached very quickly for $u \gtrsim 1$. Consequently, for $u\to 0$, $\mathcal{T}_1/\mathcal{T}_2\to 0$ irrespective of r, while for large u, i.e., in the Kondo region, $\mathcal{T}_1/\mathcal{T}_2\to 3(R/r)^2$. Thus, in the asymptotic region, where the R/r expansion makes sense, the low-temperature correction originating from the *energy* dependence of both $g_l(\varepsilon,r)$ and $G_{d\sigma}(\varepsilon+i0^+,T)$ is much larger than the one due to the temperature variation of $G_{d\sigma}(\varepsilon+i0^+,T)$ itself. Even in the Kondo limit, where $\mathcal{T}_1$ is maximal, it is of the order of the quadratic correction to the leading term of $\mathcal{T}_2$ and can therefore be neglected within the accuracy to which we know $\mathcal{T}_2$.

As for $\mathcal{T}_2$ alone, one should note that the leading term comes from the energy dependence of $g_l(\varepsilon,r)$, while only the next correction originates in the energy dependence of $G_{d\sigma}(\varepsilon+i0^+)$.

Thus, in the asymptotic region proper,

$$\delta\rho_c(r,T)\simeq\delta\rho_c^F(r)[1-\tfrac{1}{6}(k_F r)^2(\pi k_B T/\varepsilon_F)^2+\cdots]\ . \tag{43}$$

This low-T asymptotic expression is valid if both $(k_F r)(k_B T/\varepsilon_F)\ll 1$ and $r \gg R$, that is, for

$$(k_B T/\tilde{\Delta})\sin(\pi n_d/2)\ll R/r\ll 1\ .$$

Just like Friedel's expression, $\delta\rho_c^F(r)$, the low-T correction in (43) lacks any parameter pertaining to the localized state. However, it exhibits some general features which characterize $\delta\rho_c(r,T)$ at all distances, viz., (i) that the increase of temperature reduces the amplitude of CDO, and (ii) that this effect is enhanced with increasing distance from the impurity.

On the other hand, were it only for the temperature dependence of the localized-electron Green's function, i.e., of the conduction-electron scattering matrix, one would have

$$\delta\rho_c(r,T)-\delta\rho_c(r,0)\propto(\pi k_B T/\tilde{\Delta})^2(\tilde{\chi}_{\mathrm{odd}}/\tilde{\gamma})^2[1+O(R/r)] \tag{44}$$

for $r \gg R$, with $\bar{\chi}_{\rm odd}/\tilde{\gamma} \to 1$ in the Kondo limit. That is what Grüner and Hargitai[5] and Zlatić and Grüner[48] obtained assuming the low-temperature $G_{d\sigma}(i0^+,T)$ in the Fermi-liquid form

$$G_{d\sigma}(i0^+,T) = -(i/\Delta)[1 - \tfrac{1}{2}(\pi k_B T/\tilde{\Delta})^2 + \cdots]$$

and neglecting the contribution of the energy variation of $g_l(\varepsilon,r)$ and $G_{d\sigma}(\varepsilon+i0^+,T)$, which manifests itself through the Sommerfeld expansion of the Fermi integral in (14). We have shown, however, that at distances $r \gg R$, where the asymptotic expansion is valid at all, the latter contribution is larger by the factor of $(r/R)^2$.

One should bear in mind that the above conclusions, based on the large-r expansions of $\mathcal{T}_1$ and $\mathcal{T}_2$, are valid for the asymptotic region proper, i.e., when $r \gg R$. For smaller distances, $r \lesssim R$, the term $\mathcal{T}_1$ could become comparable to $\mathcal{T}_2$ or even dominant, as suggested by the *experimental* results of Grüner and Hargitai[5] and Grüner,[6] which point to the low-temperature behavior of $\delta\rho_c(r,T)$ of the form (44). The distances for which such a behavior has been observed are determined by the nature of the experimental method (continuous-wave NMR)[3] which measures the averaged-out effect of "distant" shells of host nuclei. Beyond the tenth neighbors' shell the quadrupole interactions are too small to have any discernible effect on the resulting line shape,[14] and for Al-based and Cu-based dilute alloys this corresponds to $k_F r \lesssim 16$ and 11, respectively. (See the discussion in Sec. V.) Thus, the distances contributing to the NMR signal from which the temperature dependence of $\delta\rho_c(r,T)$ was deduced are *not* asymptotic in the sense of the criterion $r \gg R$.

In summary, both the $T=0$ and low-T results indicate that any "universality" (in the sense of scaling with a single effective energy parameter like $\tilde{\Delta}$) can be expected at relatively large, but not truly asymptotic distances. These are presumably the "large distances" covered by the experimental data. For asymptotic distances, $r \gg R$, there is no local energy scale at all, while for smaller distances all energy scales are involved.

A remark on notation: In the Kondo limit, $\tilde{\Delta} \to 2k_B T_K$, where the Kondo temperature is defined as $[2\pi\chi(T=0)/(g\mu_B)^2]^{-1} \to k_B T_K$. The Bethe ansatz[36] gives $k_B T_K/\Delta = \sqrt{2u/\pi}\exp(-\frac{1}{8}\pi^2 u + 1/2u)$. The Kondo temperature of Zlatić and Grüner,[48] defined as the half-width of the Kondo resonance in $\rho_{d\sigma}(\varepsilon, T=0)$, is twice larger than T_K and coincides with the low-energy parameter Γ of Grüner and Hargitai[5] and with the Kondo limit of $\tilde{\Delta}$ of the present paper.

IV. PREASYMPTOTIC AND SMALL DISTANCES

For distances $r \lesssim R$, the approximation in which $G_{d\sigma}(\varepsilon+i0^+)$ is replaced by its values in the immediate vicinity of the Fermi energy, determined solely by n_d and $\tilde{\Delta}$, ceases to be valid. The total structure of the spectral density (SD) of local single-particle excitations, $\rho_{d\sigma}(\varepsilon) = \mp\pi^{-1}{\rm Im}G_{d\sigma}(\varepsilon \pm i0^+)$, is reflected in $\delta\rho_c$, and the CD perturbation deviates rather strongly from the values given by the asymptotic expression.

The relevant energy scale characterizing $\delta\rho_c(r)$ close to the impurity site, deduced from the measurements of CDO, seems to be given by Δ. However, when deducing the model parameters from the experimental data, one should have in mind that the proper theoretical value of $\delta\rho_c(r)$ in the preasymptotic region has to be evaluated with both the self-energy corrections and the exact form of $g_l(\varepsilon,r)$ taken into account. Note also that for the intermediate distances two energy scales, $k_B T_K$ and Δ, appear in the problem, which gives rise to the nonuniversal behavior of local properties. Therefore, when discussing the general r and T dependence of CDO, one cannot simply characterize the system by T_K. Rather, one has to choose a few representative points in the parameter space and follow their particular r and T dependence.

In the following, CDO are evaluated for the model parameters $u=2.5$ and $n_d=1$, 0.7, and 0.3. Such a choice is justified by our previous analysis[32–35] which has shown that it samples all the relevant parts of the parameter space: the Kondo region, the valence-fluctuating region, and the nearly-empty-orbital region. We take $\varepsilon_F/\Delta = 10$, which is supposed to be a reasonable estimate for <u>Al</u>3*d* and <u>Cu</u>3*d* alloys, and, accordingly, we evaluate $\delta\rho_c(r,T)$ for $l=2$, i.e., with the function $g_2(\varepsilon,r)$ given by Eq. (19).

The parameters $n_d=1$ and $u=2.5$ lead to a typical Kondo behavior. The SD has a triply-peaked shape: a narrow Kondo peak of half-width $\tilde{\Delta}$ at ε_F and two broad wings of half-width Δ at ε_f and $\varepsilon_f + U$.[26,31,34,35] Numerical results for $\delta\rho_c$ obtained with $n_d=1$, $u=2.5$ and for various temperatures are shown in Fig. 2 for distances corresponding to the first few neighboring shells (~ 10 for Al and ~ 20 for Cu). Friedel's asymptotic expression is shown by the dashed line. For larger distances, $k_F r > 4\pi$, the envelope of $\delta\rho_c(r)$, just like Friedel's expression, nearly follows the $1/r^3$ law over many lattice spacings, but with an amplitude which is smaller than in the asymptotic region. As shown in Sec. III, for Kondo systems the asymptotic form is obtained only for distances much larger than $k_F R = (\varepsilon_F/\Delta)\tilde{\gamma}$, and with $\varepsilon_F/\Delta = 10$ and $\tilde{\gamma}(u=2.5, n_d=1) = 7.166$ one has $k_F R = 71.66$.

The reduction of $\delta\rho_c$ below Friedel's values takes place here mainly because the oscillating function $g_2(\varepsilon,r)$ deviates from the exponential form used to obtain Friedel's expression. Although the effect of fluctuations for $u=2.5$ is clearly seen in the SD, which is radically different from its $u=0$ Lorentzian form, CDO do not show an appreciable modification as u is increased from 0 to 2.5. This is just the opposite of what is obtained from the asymptotic expressions (27) and (27′), where the reduction of the amplitude of CDO from Friedel's values is mainly due to the energy dependence of the scattering matrix, enhanced by the local Coulomb correlation ($\tilde{\gamma}$), while the influence of the "nonasymptoticity" of $g_l(\varepsilon,r)$ is smaller by the factor of r_l/R. The observed insensitivity of $\delta\rho_c(r,0)$ at small distances to the increase of u seems to be the peculiarity of the symmetric case, since already for $n_d = 0.9$ one obtains a notable u dependence of the CDO amplitude.

It would be interesting to study the behavior of $\delta\rho_c(r,T)$ in the limit $n_d=1$ and $u \to \infty$, but the second-

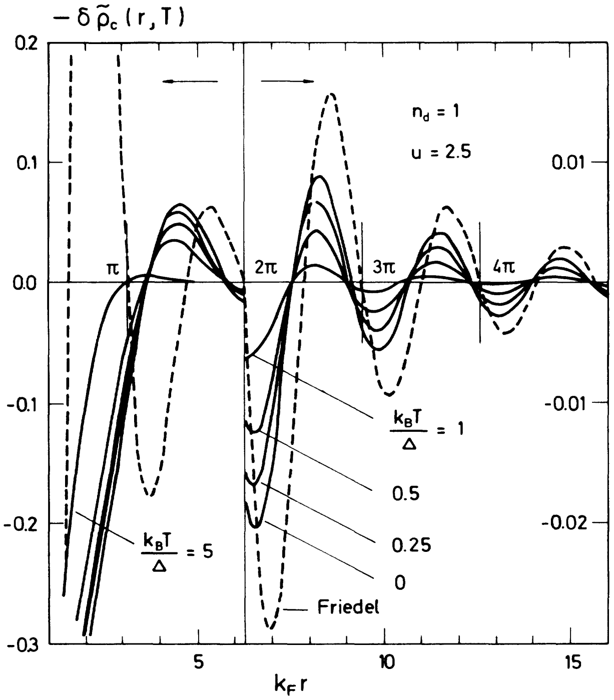

FIG. 2. $-\delta\tilde{\rho}_c(r,T)$ plotted as a function of k_Fr for $n_d=1$, $u=2.5$, and $k_BT/\Delta=0$, 0.25, 0.5, 1, and 5. The dashed line is the corresponding result of Friedel, $-\delta\tilde{\rho}_c^F(r)=(\varepsilon_F/\Delta)\sin(\pi n_d/2)\cos(2k_Fr+\pi n_d/2)/(k_Fr)^3$, with $n_d=1$ and $\varepsilon_F/\Delta=10$.

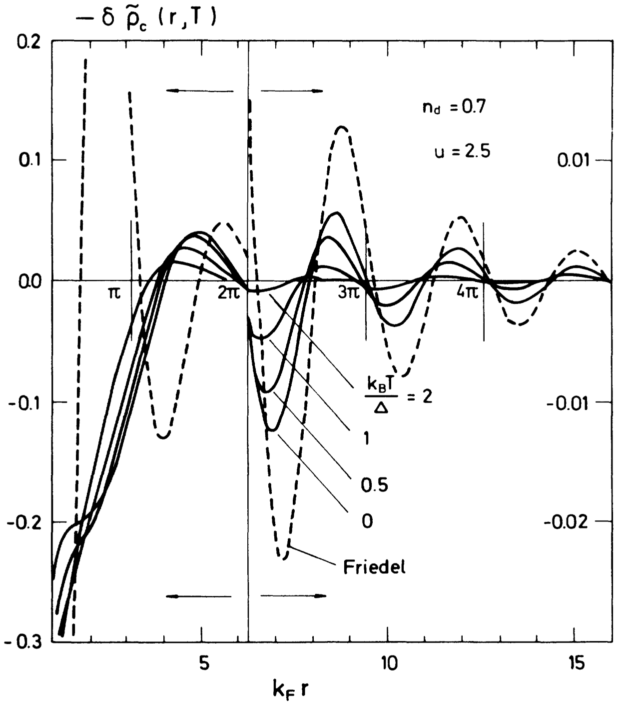

FIG. 3. $-\delta\tilde{\rho}_c(r,T)$ plotted as a function of k_Fr for $n_d=0.7$, $u=2.5$, and $k_BT/\Delta=0$, 0.5, 1, and 2. The dashed line is the corresponding result of Friedel with $n_d=0.7$.

order approximation for $\tilde{\Sigma}_{d\sigma}$ does not allow one to increase u much beyond $u\approx 2$. We do not expect, however, that further increase of u would result in qualitative changes, since $u=2.5$ (for $n_d=1$) is well within the Kondo region and exhibits all the relevant features.

The effect of temperature on $\delta\rho_c$ is also shown in Fig. 2 for a few values of k_BT/Δ. The increase of temperature decreases the amplitude of $\delta\rho_c$ and the analysis shows that the relative temperature change of $\delta\rho_c(r,T)$ increases with increasing distance. The calculation for $k_BT/\Delta=5$ shows that, except for $k_Fr\lesssim 2\pi$, CDO are completely suppressed.

The parameters $n_d=0.7$ and $u=2.5$ lead to the valence-fluctuating features of the model. The charge susceptibility of localized electrons is enhanced[33,34] and the SD exhibits two peaks of half-width $\sim\Delta$ at ε_d and ε_d+U.[34,35] These typical valence-fluctuating features are the consequence of the Coulomb correlation which also influences CDO around the impurity. Numerical results for $\delta\rho_c$ evaluated at various temperatures are shown in Fig. 3, together with Friedel's expression (dashed line). The reduction of $\delta\rho_c$ below the values given by the asymptotic expression and the shift in the phase of oscillations are clearly seen.

Temperature reduces $\delta\rho_c$, the relative change again increasing with increasing distance. However, for a given distance, the relative variation of $\delta\rho_c(r,T)$ as a function of temperature is slower for the valence fluctuating than for the Kondo systems.

The parameters $n_d=0.3$ and $u=2.5$ lead to the behavior typical of the nearly-empty-orbital regime. Here, for $\varepsilon<0$, the spectral density at $T=0$ is almost identical with the result obtained for $u=0$ (and the same value of n_d). The effects of correlation are small and the differences between the $u=2.5$ and $u=0$ results appear only for energies $\varepsilon>0$,[34,35] which do not contribute to $\delta\rho_c$ at $T=0$. Therefore the difference between the "exact" and the Hartree-Fock (or $u=0$) result for $\delta\rho_c(r,T)$ could appear for $k_BT\gg\Delta$ only.

The numerical results for $\delta\rho_c(r,T)$ are shown in Fig. 4 for various temperatures. The dashed line in Fig. 4 is Friedel's result. The effect of temperature on $\delta\rho_c$ in the nearly-empty-orbital regime increases with distance, but is rather small, as expected.

In summary, the data plotted in Figs. 2–4 show that the relative temperature variation of $\delta\rho_c(r,T)$ increases with increasing distance from the impurity for a given n_d, and decreases with increasing asymmetry (deviation of n_d from unity) for a given r. However, the difference between the relative temperature changes of $\delta\rho_c(r,T)$ for various n_d's is found to diminish with increasing distance, and presumably vanishes completely in the asymp-

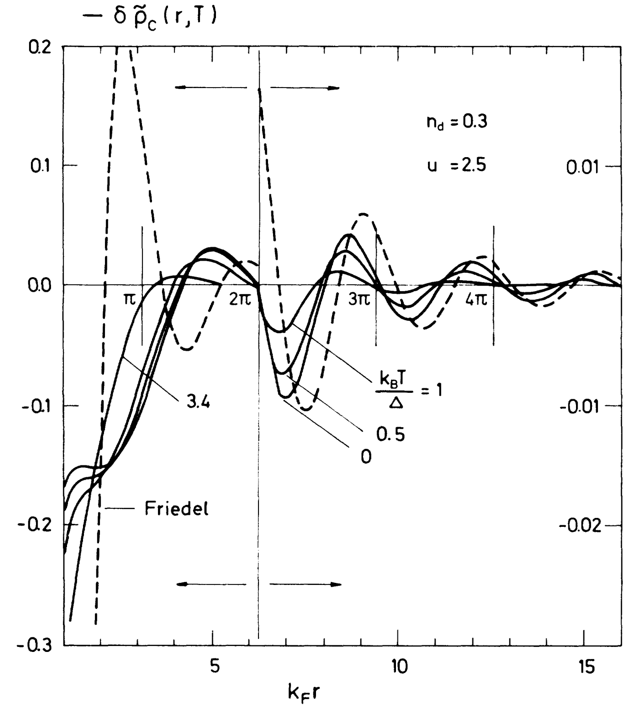

FIG. 4. $-\delta\tilde{\rho}_c(r,T)$ plotted as a function of k_Fr for $n_d=0.3$, $u=2.5$, and $k_BT/\Delta=0$, 0.5, 1, and 3.4. The dashed line is the corresponding result of Friedel with $n_d=0.3$.

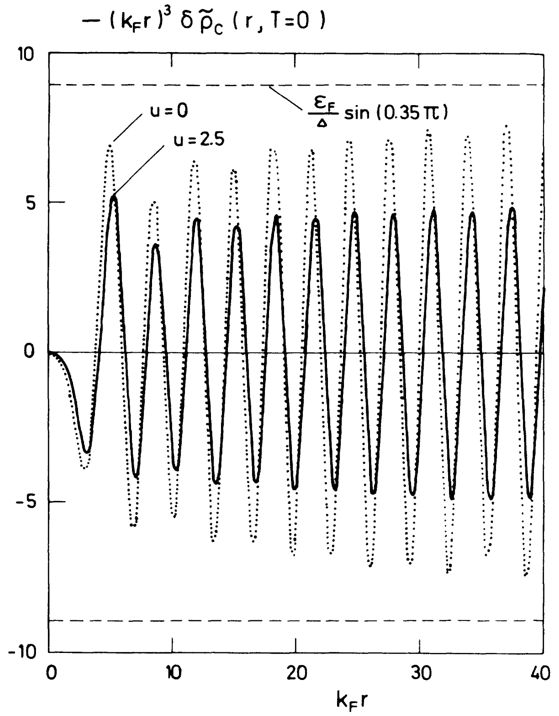

FIG. 5. $-(k_Fr)^3\delta\tilde{\rho}_c(r,T=0)$ plotted as a function of k_Fr for $n_d=0.7$, $u=2.5$ (solid line), and $u=0$ (dotted line). The dashed line is the envelope of Friedel's result.

totic region, as indicated by the low-temperature expansion (43) which gives

$$[\delta\rho_c(r,T)/\delta\rho_c(r,0)]-1=-\tfrac{1}{6}(k_Fr)^2(\pi k_BT/\varepsilon_F)^2\ ,$$

an expression lacking any n_d dependence.

Furthermore, the strong dependence of the temperature effect on distance shows clearly that there is no factorization of $\delta\rho_c(r,T)$ into a temperature-dependent and a distance-dependent term. Such a separation would necessarily imply a distance-independent temperature variation of $\delta\rho_c(r,T)$, contrary to what is observed in Figs. 2–4. The low-temperature asymptotic expression (43) shows that such a factorization cannot be expected to occur even for large distances from the impurity and at low temperatures.

To study the effect of the Coulomb correlation and the approach of the oscillations towards the asymptotic form in more detail, in Fig. 5 we have plotted the quantity $(k_Fr)^3\delta\rho_c(r,0)$ as a function of k_Fr for the case $n_d=0.7$. In such a way the behavior of the oscillations can be followed in a large k_Fr interval since the decrease of $\delta\rho_c(r,0)$ for $k_Fr \gtrsim 4\pi$ is described rather accurately by the (k_Fr^{-3}) power law. The dashed line in Fig. 5 is the envelope of Friedel oscillations and the dotted line is the result obtained for $n_d=0.7$ but for $u=0$. Thus, the systems with the same local charge but different spectral densities, a double-peaked structure for $u=2.5$ and a simple Lorentzian for $u=0$, are compared. Note that even for systems without any Coulomb correlation, the charge density approaches the asymptotic form very

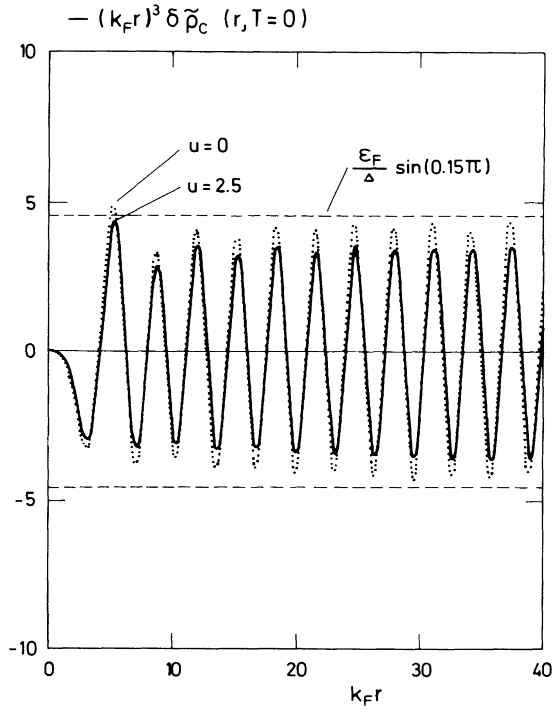

FIG. 6. $-(k_Fr)^3\delta\tilde{\rho}_c(r,T=0)$ plotted as a function of k_Fr for $n_d=0.3$, $u=2.5$ (solid line), and $u=0$ (dotted line). The dashed line is the envelope of Friedel's result.

slowly if the full expression (19) for g_2 is used in Eq. (14). The difference between the curves evaluated with $u=2.5$ and $u=0$ shows how the correlation reduces the magnitude of $\delta\rho_c(r,0)$ and pushes the onset of the asymptotic behavior to much larger distances. Although the expression $(k_F r)^3\delta\rho_c$ oscillates around the impurity with an amplitude which is nearly constant over many lattice spacings, it is clear that the *asymptotic* expression is not valid for valence-fluctuating systems in any region of physical interest. It is only in the case of a nearly empty orbital that the asymptotic form is approached rather rapidly, with the envelope of $(k_F r)^3\delta\rho_c$ becoming constant and equal to that of Friedel's expression for $k_F r \gg \max\{(\varepsilon_F/\Delta)\sin(\pi n_d/2), l(l+1)+\frac{1}{2}\}$, which is not very large. For the case $n_d=0.3$, shown in Fig. 6, the asymptotic radius amounts to some $6k_F^{-1}$, since (with our standard choice of parameters) $k_F R=5.2\sim k_F r_2=6.5$.

V. THEORY AND EXPERIMENT

Finally, we would like to comment on the relevance of our results for the understanding of the experimental data. To that end, we first briefly review the experimental methods used to investigate CDO in dilute alloys, to appreciate their capabilities and limitations, and discuss some problems pertaining to the interpretation of the experimental data and their linkage with theory.

Experimentally, charge-density perturbation around transition-metal or rare-earth impurities in normal-metal hosts is studied most effectively by the continuous-wave nuclear magnetic resonance[1-6] (cw NMR) and the pure nuclear quadrupolar resonance (NQR) using the field-cycling technique,[7-13] but other methods like Knight-shift measurements[15-18] are extensively used as well. While the first two methods provide information on the total distribution of the screening charge density, including all the electrons corresponding to different l states, the third one reflects the contribution from the s states only[14] (provided one excludes the contribution of core polarization).

In a pure metal with cubic symmetry, the electric field gradient (EFG) on each nucleus is equal to zero and the $2I+1$ Zeeman nuclear energy levels are equally spaced, leading to a single absorption line. In a dilute alloy, the redistribution of the electronic charge around an impurity, $\delta\rho_c(\mathbf{r})$, destroys the cubic symmetry of the host and gives rise to the EFG which interacts with the quadrupole moments of the surrounding host nuclei, causing shifts in the nuclear energy levels and the consequent changes of the quadrupolar transition frequencies. Each successive shell of the host nuclei around the impurity experiences the *local* value of the EFG, which shifts the position and modifies the shape of the NQR lines corresponding to that shell. The cw NMR then detects either the weak satellite lines in the vicinity of the main line, arising from the quadrupolar couplings acting as a perturbation on the Zeeman coupling in the external magnetic field or, for larger distances from the impurity, the change in intensity and shape of the main line, arising from the averaged-out effect of distant shells. The pure NQR, on the other hand, detects transitions between nuclear levels split only by the EFG, in zero external magnetic field. Using cw NMR and pure NQR as complementary techniques, one can extract information on the values of the EFG up to some 10 shells of the host nuclei surrounding the impurity, and these values can then be related to the spatial distribution of the screening charge, $\delta\rho_c(\mathbf{r})$. Neither of these two steps is straightforward.

As for the second one, the EFG is, in general, a *functional* of $\delta\rho_c(\mathbf{r})$. Kohn and Vosko[20] have found

$$q(\mathbf{r})=-\int d^3r'\frac{\delta\rho_c(\mathbf{r}+\mathbf{r}')}{|\mathbf{r}'|^3}[3(\hat{r}\cdot\hat{r}')^2-1][1+\gamma(r')]\ , \tag{45}$$

where $\gamma(r')$ is the so-called antishielding factor. For large distances from the impurity this functional reduces to the simple linear relationship

$$q(r)\rightarrow(8\pi/3)\mu\delta\rho_c^F(r)\ , \tag{46}$$

where μ is the core enhancement factor depending on the host, which measures the increase of $q(r)$ over its value in a plane-wave theory without antishielding. For small distances from the impurity, the discrepancies between the experimental values of $q(r)$ and those given by Eq. (46) can originate *both* in the deviation of the true $\delta\rho_c(r)$ from its asymptotic form $\delta\rho_c^F(r)$ *and* in the fact that the linear relationship between $\delta\rho_c(r)$ and $q(r)$ simply does not hold at small distances. Nevertheless, relation (46) has been extensively used in the interpretation of experimental data even for small distances, where its justification is doubtful, under the tacit assumption that the former effect is dominant, while the latter one can be neglected. That is, the experimental values of $q(r)$ have been compared with those given by

$$q(r)=(8\pi/3)\mu\delta\rho_c(r)\ , \tag{47}$$

where the local linear relationship (46) between the EFG and the CD perturbation was extrapolated to small distances, while the asymptotic expression $\delta\rho_c^F(r)$ was substituted by the best currently known theoretical expression for $\delta\rho_c(r)$.

To estimate the range of $k_F r$'s covered by the experimental data obtained on the aluminum- and copper-based dilute alloys, one should recall that both aluminum and copper crystallize in the FCC lattice, with lattice constants $a_{\mathrm{Al}}=7.6371a_H$ and $a_{\mathrm{Cu}}=6.8170a_H$ (where $a_H=\hbar^2/me^2$ is the Bohr radius). The radii of the first and tenth neighbors' shell in the FCC lattice are $a/\sqrt{2}$ and $a\sqrt{5}$, respectively. With the free-electron estimates of the Fermi wave vector, $k_F^{\mathrm{Al}}=0.9245a_H^{-1}$ and $k_F^{\mathrm{Cu}}=0.7173a_H^{-1}$, one obtains $k_F r_1=4.99$ (3.46) and $k_F r_{10}=15.79$ (10.93) for aluminum (copper). Thus, any available experimental data refer to the distances $5\lesssim k_F r\lesssim 16$ for Al-based and $3.5\lesssim k_F r\lesssim 11$ for Cu-based dilute alloys. In both cases this falls short of the asymptotic region as defined by $r\gg R$, at least for "magnetic" alloys (which are the interesting ones). Moreover, the *local* values of the EFG can be determined only for the first four or five neighboring shells, which should be regarded as small distances, while the "wipe-out number" experiments, which give only the averaged-out amplitude of CDO, reach up to the intermediate (preasymptotic, $r \sim R$) distances at best.

For such distances one should not rely on the simple linear dependence (47) of the EFG on $\delta\rho_c(r)$, which is certain to hold only in the asymptotic region. Instead, one should return to the original expression (45) for the EFG as a functional of $\delta\rho_c(r)$, as already suggested by Fukai and Watanabe[49] and Berthier.[50] Also, the data obtained for largest distances accessible to experiment should not be simply taken as "asymptotic." This particularly refers to the "wipe-out number" results for the temperature dependence of CDO.

On the theoretical side, one should bear in mind that, in a real alloy, many effects can be comparable to or even stronger than those due to the many-body processes modeled by the Anderson (or any similar) Hamiltonian. We have seen that even the theoretical results for $\delta\rho_c(r)$ at small distances ($k_F r \lesssim 4\pi$) are rather strongly model dependent as regards the assumptions about the band structure of the host and its hybridization with the impurity orbital.[51] In addition, the experimental results of Minier and Ho Dung[13] on various impurities in aluminum indicate a strong anisotropy of the CD perturbation, presumably due to the distortions of the Fermi surface of the host appearing near its intersections with the first Brillouin zone boundaries. They concluded that no theory assuming an isotropic CD perturbation can explain the values of the EFG around the impurities in Al, which may well be true if one aims at fitting the experimental data with theoretical curves.

Also, for the closest shells (first, second, and third neighbors), the phase shifts η_0 and η_1 can give a non-negligible contribution to the EFG,[10] so that the Anderson model, which is based on the dominance of a single resonant phase shift, may fail to describe the local properties correctly in the immediate vicinity of the impurity.

Thus, the present state of the theory does not allow a serious quantitative comparison with the experimental results. Nonetheless, the extensive experimental work on the aluminum-based 3*d* alloys[2–13] allows one to conclude that the main *qualitative* features seen in the data are reproduced by the theory. As shown in Refs. 10, 11, and 14, the EFG data on all the "nonmagnetic" $\underline{\text{Al}}$3*d* alloys could be consistently described by assuming that the conduction-electron scattering matrix has a Lorentzian energy dependence, as in the $U=0$ Anderson model, with $\Delta \simeq 1$ eV. For the "magnetic" $\underline{\text{Al}}$Mn and $\underline{\text{Al}}$Cr alloys, on the other hand, one would need $\Delta \simeq 0.4$ eV in order to account for the "anomalous" suppression of the preasymptotic screening charge.[11] While such a large variation of the width of the virtual bound state across the 3*d* series is hard to understand within the Anderson model, it is clear from our results that the apparent "reduction" of Δ is simply a manifestation of the strong Coulomb correlations which are also responsible for the apparent "magnetic" behavior of Mn and Cr alloys. Furthermore, the complete behavior of CDO at all distances and temperatures cannot be accounted for simply by a suitable choice of Δ within a single-particle theory. $\delta\rho_c(r,T)$ is determined by the total energy spectrum, which has a more complicated structure than a Lorentzian of half-width Δ. Finally, the low-temperature scale defined by the EFG data of $\underline{\text{Al}}$Mn and $\underline{\text{Al}}$Cr alloys in the preasymptotic region agrees, more or less, with the one defined by the transport or thermodynamic measurements,[6,14] which is also obtained in our calculations. Specifically, our large-$k_F r$ results show the existence of a low-temperature term proportional to $(T/T_K)^2$, which is dominated by other corrections in the asymptotic region, but seems to become the leading one for $r \sim R$.

VI. CONCLUSIONS

In summary, we have shown that the CDO in the conduction band can be significantly affected by the Coulomb interaction between localized electrons, but also by the specific form of the function $g_l(\varepsilon,r)$ which depends rather strongly on the properties of the hybridization matrix element and the pure-host conduction states. The latter effect is most pronounced for relatively small distances from the impurity, that is, just in the region accessible to experiment. This has to be kept in mind when estimating the parameters of the Anderson model from the NMR data taken at the host nuclei.

Although the Hartree-Fock theory, which takes into account the energy dependence of the conduction-electron scattering matrix, substantially improves upon Friedel's asymptotic result, it still overestimates the value of $\delta\rho_c$ in the preasymptotic region, except for $n_d \ll 1$ or $2-n_d \ll 1$. The onset of the asymptotic behavior, predicted by the Hartree-Fock theory at about $k_F R_{\text{HF}} = (\varepsilon_F/\Delta)\sin(\pi n_d/2)$, is pushed by the correlation effects to the distances $r \gtrsim R = \tilde{\gamma} R_{\text{HF}}$. The MB enhancement factor $\tilde{\gamma}$ can be considerably larger than unity.

Temperature reduces the amplitude of CDO, and this effect is enhanced with increasing distance from the impurity and decreases with asymmetry. The latter decrease (n_d dependence) becomes weaker for larger distances and presumably vanishes in the asymptotic region, as indicated by the analytical low-temperature results. There is no factorization of the spatial and temperature dependence of $\delta\rho_c(r,T)$ even in the asymptotic region, let alone for smaller distances from the impurity.

Both the $T=0$ and low T results indicate that any "universality," i.e., scaling with a single effective energy parameter like T_K, can be expected at relatively large ($r \sim R$), but not asymptotic ($r \gg R$) distances. For $r \to \infty$ there is no local energy scale at all, while for $r \ll R$ all energy scales are involved. Thus, the space around the impurity can be divided into three regions, viz., the asymptotic region proper, for $r \gg R$, the preasymptotic region, around $r \sim R$, and the region of small distances, for $r \ll R$.

In view of this division, the experimental data on CDO around 3*d* or 4*f* impurities in normal metals cover the distances up to $r \lesssim R$ only, at least for the "magnetic" alloys, which exhibit the "anomalous" behavior and have aroused interest in the first instance. On the other hand, the model we use is too coarse to take into account all the effects that may significantly influence the CDO in real alloys. Therefore, a serious quantitative comparison between the theoretical and experimental results still cannot be made, but the main qualitative features of the experimental data are reproduced by the theory.

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