Theory of Anomalous Charge Oscillation around Resonant Scattering Impurities

F. Mezei* and G. Grüner†
Central Research Institute for Physics, Budapest, Hungary
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A theory of the charge-density oscillation around resonant scatterers is presented which explains the recent experimental results on the anomalous charge perturbation around transition-metal impurities in Al and Cu. Its application to the Kondo effect suggests a crucial test for the existence of the Kondo resonance, and shows that available NMR data rule out the validity of the Kondo model for Al–3*d*-transition-metal alloys, while further experiments are proposed to answer this question in the case of Cu-based alloys.

Friedel's classical asymptotic formula[1] for the charge-density oscillation around a scattering center within an electron gas was derived by neglecting the energy dependence of the phase shifts describing the scattering. This approximation can be expected to be fairly good for non-transition-metal impurities in simple metal hosts, for which the series-expansion treatment of the realistic smooth energy dependence of the phase shifts results in only minor corrections affecting the phase of the oscillation in practice at only the first few neighboring shells around the impurity.[2] In the case of *d*–transition-metal impurities, however, the existence of the virtual bound state (vbs) near the Fermi energy will result in a drastically energy-dependent *d*-type scattering, and a serious deviation is found both from Friedel's simple formula and from refined theories.[2] In fact, extensive NMR studies of the charge perturbation around a great variety of nonmagnetic impurities in Cu and Al have shown a general behavior in accordance with these expectations. Namely, the following has been established by NMR measurements made on the host nuclei:

(i) The charge-density oscillation at a distance of about 14–24 Å from the impurity, as sensed by the first-order quadrupole effect showing wipe-out numbers of 500–2500, can be fairly well accounted for even quantitatively by Friedel's asymptotic expression for all kinds of impurities concerned.[3]

(ii) The charge-density oscillation at distances below about 8 Å, measured by the second-order quadrupole effect[4] (wipe-out numbers between 20 and 100) and by the pure quadrupole resonance of the nuclei in the first few neighboring shells,[5,6] has an amplitude for *d*–transitional-metal impurities which is strongly depressed as compared with the values given by the Friedel formula, while there is no such deviation for other impurities.

The primary aim of the present work was to determine on more rigorous theoretical grounds the behavior of the charge-density oscillation around a single resonant scatterer in order to find an explanation for the anomaly mentioned in (ii). The results obtained compare favorably with experimental findings. On the other hand, by connecting the rate of the deviation from the Friedel asymptotic expression to the energy width of the resonance scattering, our results show that the investigation of the anomalous charge-density oscillation is a unique tool for obtaining direct information about the energy dependence of the impurity scattering amplitude at a given temperature, in contrast to the investigation of the transport properties at different temperatures, for which case the energy and temperature dependence of the scattering amplitude are inseparably mixed together. Thus, our theory suggests an important possibility of looking for the sharp Kondo resonance in a direct way.

The calculations utilize a method described in more detail by Mezei and Zawadowski.[7] The local density of states for the conduction electrons is determined using the one-particle thermodynamic Green's function as $\rho(\vec{r}, \omega) = -\pi^{-1}\,\mathrm{Im}[G(\vec{r}, \vec{r}; \omega + i\delta)]$, where $\vec{r}$ is the position vector measured from the impurity, and $G(\vec{r}, \vec{r}; \omega)$ is determined in the usual way by the free-electron Green's function, corresponding to the effective mass m^*, and by the spin-nonflip scattering amplitude $t_l(\omega)$, corresponding to a single angular-momentum quantum number l (nonresonant *s*- and *p*-type scattering being neglected throughout). In later calculations the reasonable assumption will be made that $t_l(\omega)$ has a Lorentzian form,

$$t_l(\omega) = \frac{1}{\pi\rho_0}\,\frac{\Delta}{\omega - \omega_0 + i\Delta}, \tag{1}$$

ρ_0 being the unperturbed conduction-electron density of states for one spin direction at the resonance energy ω_0. It is assumed that the width of the resonance is small compared to the Fermi energy, $\Delta \ll \epsilon_F$, and that the resonance is near the Fermi energy, $\omega_0 \ll \epsilon_F$. (For the related problem of the less-pronounced density-of-states anomalies expected as a result of the dependence of the t matrix on the absolute value of the momenta, see Ref. 7.)

In order to calculate the total charge density oscillation, $\rho(\vec{r}, \omega)$ is first evaluated along the straightforward lines suggested in Ref. 7 and then integrated over the occupied states, substracting the unperturbed uniform charge density ($r = |\vec{r}|$):

$$\Delta\rho(r, T) = \int_{-\epsilon_F}^{\infty} (2l+1)\pi^{-1} \mathrm{Im}\{t_l(\omega)[G_l(r; \omega + i\delta)]^2\} f(\omega)\, d\omega, \tag{2}$$

where $f(\omega)$ is the Fermi function and G_l is the lth angular-momentum component of the free-electron Green's function, given by

$$G_l(r; \omega + i\delta) = -(m^*/2\pi r)[ik_\omega r h_l^{(1)}(k_\omega r) - p_l/r^2 k_\omega^2],$$

in which $k_\omega = [2m^*(\omega + \epsilon_F)]^{1/2}$, p_l is a constant, e.g., $p_2 = 3$, and $h_l^{(1)}$ is a spherical Bessel function of the third kind,[8] approximated further on for $x \gg 1$ according to the relation $x h_l^{(1)}(x) \simeq i \exp[ix - \frac{1}{2}l\pi + \varphi(x)]$. Here the phase correction $\varphi(x)$ for $l = 2$ is given by $\varphi = 3/x$. Evaluating now the integral (2) using the Bethe-Sommerfeld approximation, we get

$$\Delta\rho(r, T) = \Delta\rho(r, 0) - (2l+1)(m^*/2\pi r)^2 \tfrac{1}{6}\pi (k_B T)^2 \mathrm{Im}\{(d/d\omega)[t_l(\omega) \exp(2i[k_\omega r - \tfrac{1}{2}l\pi + \varphi(k_\omega r)])]\}_{\omega=0}, \tag{3}$$

with T being the temperature and

$$\Delta\rho(r, 0) = -(2l+1)(m^*/2\pi r)^2 \pi^{-1} \mathrm{Im} \int_{\epsilon_F}^{0} t_l(\omega) \exp(2i[k_\omega r - \tfrac{1}{2}l\pi + \varphi(k_\omega r)])\, d\omega. \tag{4}$$

It is one of our basic points to observe that the Friedel asymptotic formula is valid as the limiting case of integral (4) for large enough distances r, namely, for $r \gg \xi_\Delta$, where the coherence length $\xi_\Delta = v_F/2\Delta$ is defined in a way analogous to that known from the theory of superconductivity [$v_F = (dk_\omega/d\omega)_{\omega=0}^{-1}$ is the Fermi velocity]. This is seen by noting that for $r \gg \xi_\Delta$, the term $\exp(2ik_\omega r)$ oscillates rapidly as a function of ω, as compared with the rate of change of $t_l(\omega)$. Thus, according to the Riemann lemma, the integral (4) vanishes except for the contribution of the sharp discontinuity corresponding to the upper limit of integration:

$$\Delta\rho(r, 0) \simeq -(2l+1)(m^*/2\pi r)^2 \pi^{-1} \mathrm{Im}\{(v_F/2ir) t_l(0) \exp[2i(k_F r - \tfrac{1}{2}l\pi)]\},$$

which, on introducing the phase shift $\delta_l(0)$ by the equation $\pi\rho_0 t_l(0) = -\sin\delta_l(0) \exp[i\delta_l(0)]$, becomes identical to the familiar Friedel formula.

In the opposite limit, $r \ll \xi_\Delta$, the integral (4) can be evaluated only from the detailed knowledge of $t_l(\omega)$. One can, however, generally claim that as r tends to zero, $\exp[2ik_\omega r]$ will be practically independent of ω over the most important range of integration around the resonance of width Δ. Thus, the integral tends to saturate as $r \to 0$ and the change of $\Delta\rho(r, 0)$ will approach, instead of Friedel's r^{-3} law, a slower varying r^{-2} law [see Eq. (4)] at a rate determined by the slowly decreasing tail of $t_l(\omega)$ far from the resonance. The range of this type of behavior is also determined by ξ_Δ, as obviously $r \ll \xi_\Delta$.

We have calculated $\Delta\rho(r, 0)$ explicitly for arbitrary r in the case of the Lorentzian resonance given by Eq. (1) and for Hamann's approximate solution for the Kondo resonance,[9] too. All further approximations that are used—namely, replacing the dispersion relation by $k_\omega = k_F + \omega/v_F$, extending the lower limit of the integration in Eq. (4) to $-\infty$, and replacing $\varphi(k_\omega r)$ by a constant $\varphi(k_F r)$—together with the previous ones, are valid for $k_F r \gg 1$, and the results will be reasonably correct even for $k_F r = 5$, i.e., at the place of the first neighbors of the impurities, too. With these approximations the integral (4) can be calculated exactly for the Lorentzian resonance and numerically for the Hamann resonance, and the result can be expressed in the form of a corrected Friedel formula as

$$\Delta\rho(r, 0) = -[(2l+1)/4\pi^2] \sin\delta_l(0)\, [a(r)/r^3] \cos[2k_F r - l\pi + \delta_l(0) + 2\varphi(k_F r) - \eta(r)].$$

The correction functions $a(r)$ and $\eta(r)$ are shown in Figs. 1 and 2. In the case of the Lorentzian resonance $a(r) = |ze^z E_2(z)|$ and $\eta(r) = \arg[ze^z E_1(z)]$ with $z = (1 + i\lambda)r/\xi_\Delta$, and $\lambda = \omega_0/\Delta$, where $E_1(z)$ is the so-

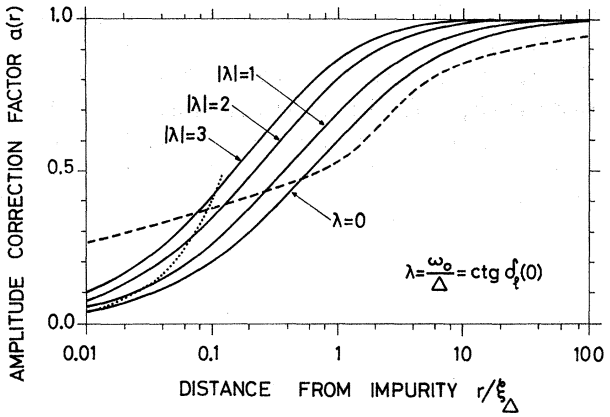

FIG. 1. Amplitude of the charge-density oscillation relative to that given by Friedel's expression as a function of the distance r/ξ_Δ for Lorentzian resonances with various resonance energies ω_0/Δ (solid lines) and for the $T_K=\Delta/k_B$ Hamann solution (dashed line). For comparison, the dotted line shows the r^{-2} law, i.e., $a(r)\propto r$.

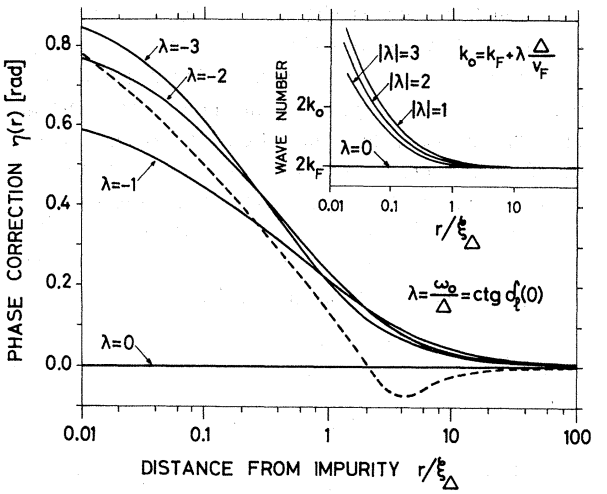

FIG. 2. Phase of the charge-density oscillation relative to that given by Friedel's expression as a function of the distance r/ξ_Δ for Lorentzian resonances with various resonance energies ω_0/Δ (solid lines) and for the $T_K=\Delta/k_B$ Hamann solution (dashed line). The inset shows the change of the wave number of the oscillation.

called exponential integral function[8]; note that $a(r)$ and $\eta(r)$ are even and odd functions of λ, respectively, i.e., for $\omega_0=0$, $\eta(r)$ vanishes. Because of the r dependence of $\eta(r)$, the wave number of the oscillation deviates from the familiar value $k_F r$, as shown in the inset of Fig. 2. It is seen that in both cases the qualitative behavior of $a(r)$ corresponds to our previous general conclusions, demonstrating a fair independence of the particular shape of the resonance, as expected.

Furthermore, evaluating Eq. (3) for the Lorentzian resonance concerned, we get for the temperature dependence of the charge-density oscillation directly that

$$\Delta\rho(r,T)-\Delta\rho(r,0)=\frac{2l+1}{4\pi^2}\sin\delta_l(0)\frac{1}{r^3}\frac{\pi^2(k_BT)^2}{6}r^2\left\{\left(1+\frac{\xi_\Delta}{r}\frac{\Delta^2}{\Delta^2+\omega_0^2}\right)\cos[2k_Fr-l\pi+\delta_l(0)+2\varphi(k_Fr)]\right.$$
$$\left.+\frac{\xi_\Delta}{r}\frac{\Delta\omega_0}{\Delta^2+\omega_0^2}\sin[2k_Fr-l\pi+\delta_l(0)+2\varphi(k_Fr)]\right\}. \quad (5)$$

If we replace ξ_Δ by zero, this expression reduces to that obtained by Adawi,[10] which implies a temperature dependence in phase with the Friedel oscillation. Apart from quantitative corrections, the important new feature of our result is that in the case of resonant scattering the temperature dependence includes out-of-phase contributions as well, due to the appearance of the phase correction $\eta(r)$ and of the last term in the right-hand side of Eq. (5).

Now let us turn to a discussion of these results. It is immediately clear from Fig. 1 that the anomalous behavior of the charge oscillation around transition-metal impurities that was outlined in (i) and (ii) can be explained by the present theory supposing that ξ_Δ is 5–10 Å, i.e., $\Delta=1$–0.5 eV, in convincing agreement with present estimates of the width of the vbs in Cu and Al. A detailed comparison of our theory with experimental data, however, will be given elsewhere.[11]

Here we focus attention on the implication of the present analysis for the Kondo effect. By determining an estimate of ξ_Δ from NMR investigation of the charge-density oscillation at a given temperature, one can deduce a value for the width of the resonant impurity scattering concerned. This offers a direct test of the basic result of the Kondo theories, i.e., the appearance of a resonant scattering with a width of about k_BT_K at temperatures below the Kondo temperature T_K,[12] a concept that has been widely used to interpret experimental data.[13] Consider, for example, AlMn: It is known that the temperature dependence of the macroscopic properties of this alloy can be explained by a Kondo-type resonance with a width corresponding to about 500°K.[14] On the other hand, from the first-order NMR wipe-

out number $n = 1650$ at $T = 0°K$,[15] one finds at the wipe-out distance of about 20 Å a charge-density oscillation amplitude which amounts to 80% of the value calculated[11] using Friedel's asymptotic expression with the resonance at the Fermi energy, i.e., $\delta_l(0) = \pi/2$, corresponding to the unitarity limit. (This large value of the first-order quadrupole wipe-out number can be understood only if d-wave scattering dominates over the s- and p-type scattering, in accordance with our previous assumption.) Looking now at Fig. 1, we see that in this case ξ_Δ cannot be greater than approximately half of the above radius, i.e., $\xi_\Delta \leq 10$ Å, which means that $\Delta \geq 0.5$ eV, a value close to the width of the vbs in Al-based alloys of about 0.6 eV,[13] and an order of magnitude larger than $k_B T_K$. This fact rules out the existence of a single narrow Kondo resonance, and so we are forced to assume that in the temperature dependence of the different macroscopic properties and of the charge density oscillation,[14] the temperature dependence of the scattering amplitude $t_l(0)$ plays a major role, and/or that $t_l(\omega)$ has a much more complex structure than that corresponding to a single-peaked conventional resonance, in which case our considerations have to be applied with particular care.[16]

The analysis shows the fundamental importance of determining the charge-density oscillation in the nonmagnetic regime (below T_K) of "typical" Kondo systems. Thus, we propose first of all the experimental determination of the amplitude of the charge density oscillation in the $T \to 0°K$ limit, as measured by the first-order NMR quadrupole effect, in the *Cu*Fe and *Cu*Co alloy systems. An analysis of the results along the present lines would provide a crucial test of the existence of a Kondo-type resonance in these alloys.

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*Present address: Institute Laue-Langevin, Grenoble, France.

†Present address: Imperial College, Department of Physics, London, England.

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Magnetic Structures of Samarium*

W. C. Koehler and R. M. Moon

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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The magnetic structures of metallic samarium have been determined from neutron-diffraction data on a single crystal of ^{154}Sm. Anomalies in a number of physical properties of this metal at 106 and 13.8°K are associated with ordering of the moments on the hexagonal and cubic sites, respectively. The unusual form factor expected for a $4f^5$ configuration has been observed. Striking evidence for important conduction-electron polarization effects has been found.

Anomalies in the electrical resistivity[1] and specific heat[2,3] of samarium have been detected near 106 and 14°K, which are suggestive of magnetic-ordering transitions at these temperatures. Recently, single-crystal magnetic-susceptibility data have been reported,[4] which are explicable if Sm at 4.2°K is a c-axis antiferromagnet. Up until now, neutron-diffraction studies of this metal