Electronic stabilization of amorphous and quasicrystalline metals: Importance of quantum correlations

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Abstract

Numerous experimental indications suggest that the Hume-Rothery mechanism plays an important role in stabilizing quasicrystalline and amorphous phases. However, the exponential damping of the conventional Friedel oscillations at the relevant, elevated temperatures $T$ poses a severe challenge to the HR stabilization. In order to resolve this problem it is shown using a Feynman diagram technique that quantum correlations in the electron sea, arising from the interplay of Coulomb interaction and impurity scattering, can strongly enhance the Friedel oscillations in these systems even at elevated temperature. The resulting corrections to the Friedel potential are in agreement with available experimental results on amorphous HR alloys. It is proposed to include the enhancement of the Friedel amplitude derived in the present work into pseudopotentials through the local field factor.

Keywords: Electronic structure; Coulomb interaction and disorder; screening; Friedel oscillations.

1. Introduction

The microscopic origin of the stability of quasicrystalline phases continues to be an unresolved issue. While at high temperatures the long-range order of quasicrystals and approximants may be favored over crystalline order because of entropic effects, striking interrelations between the ionic and the electronic structures especially in icosahedral (i) quasicrystals seem to indicate that electronic stabilization plays an important role at short and intermediate length scales of of several atomic spacings: (1) The electron density of states (DOS) has a pronounced, structure-induced pseudogap at the Fermi level $\varepsilon_F$. (2) The position $k_p$ of the main ionic structural peak coincides with twice the Fermi wave number, $2k_F \simeq k_p$. (3) In dependence of the composition from their constituents, quasicrystalline phases are only stable in small regions where the condition $2k_F \simeq k_p$ is satisfied. (4) In the quasicrystalline phase the electrical resistivity is substantially larger than that of each of the elemental constituents. Similar coincidences between electronic and ionic structures are observed in amorphous noble-polyvalent alloys. These findings may be traced back to the common feature of these materials that the ion system exhibits concentrical, shell-like density correlations, where the spacing $a$ between neighboring shells coincides with the Friedel wavelength, $\lambda_F \equiv \pi/k_F = 2\pi/k_p \equiv a$. Therefore, it has been conjectured that the electronic Friedel oscillations around an arbitrary central ion give an important contribution to the pair potential. As a consequence, the total energy of the system should be optimized by the ions effectively being bound in the minima of the Friedel potential and a concommitant pseudogap formation at $\varepsilon_F$. The importance of such a Hume-Rothery (HR) stabilization mechanism is supported by detailed theoretical studies at temperature $T = 0$ both for amorphous and for quasicrystalline systems. Numerical simulations show that quasicrystalline structures can indeed be grown by the use of pair potentials with appropriate repulsive (i.e. oscillatory) parts.

However, at the relevant temperatures where quasicrystals or amorphous structures are stable ($T \simeq 10^2 \ldots 10^4 K$), regular Friedel oscillations are expo-
2. Model and effective interaction

We here discuss an effective model for the electron motion in amorphous and quasicrystalline systems at \( T > 0 \). The ionic density correlations mentioned above constitute a scattering potential for the electrons whose scattering T-matrix \( t_{\vec{k},\vec{k}'} \) is, by definition, proportional to the static ion structure factor, \( t_{\vec{k},\vec{k}'} \propto S(|\vec{k} - \vec{k}'|) \), which in turn is peaked at a momentum transfer \( q \equiv |\vec{k} - \vec{k}'| = k_p \approx 2k_F \) and thus leads to enhanced backscattering. As has been shown \[18, 19, 20\], the latter not only generates a pseudogap but at the same time leads to a substantial increase of the electron transport or density relaxation rate, \( \tau^{-1} \), over the quasiparticle decay rate, \( \tau_{qp}^{-1} \). \( \tau^{-1} > \tau_{qp}^{-1} \) is a generic feature of the amorphous and the quasicrystalline state. In quasicrystals, when the conductivity is substantially reduced below the Drude result, we may have \( \tau^{-1} \gg \tau_{qp}^{-1} \).

In addition, at the relevant, finite temperatures the phase coherence of the electrons is lost on the length scale of the inelastic mean free path. It follows that the electrons cannot probe the long-range order in a quasicrystal. Rather, they experience an effective potential made up of randomly placed, spatially extended scattering centers, each one characterized by the T-matrix \( t_{\vec{k},\vec{k}'} \). In such a potential the electronic motion is diffusive instead of ballistic, similar as in amorphous metals. When the electron coherence length is long enough (low \( T \)), the motion may be subdiffusive with a diffusion exponent \( \beta < 1/2 \). However, for the present purpose the precise value of \( \beta \) is unimportant, and we will assume \( \beta = 1/2 \) (classical diffusion) in the following.

Diffusion, as a dissipative process, is difficult to incorporate in an \textit{ab initio} calculation. Therefore, we will choose a Feynman diagram technique, where diffusion arises by averaging over all (quasi-)random configurations of the system. In a diffusive electron sea screening is inhibited, so that the effective Coulomb interaction, \( v^{eff}_{\vec{q}}(z, Z) \), between electrons with complex frequencies \( z \) and \( z + Z \) acquires a long-range, retarded part \[1\],

\[
v^{eff}_{\vec{q}}(z, Z) = v_0 \Gamma^2(z, Z, q) e^{RPA}(Z, q), \quad v_0 = 4\pi e^2/q^2., \tag{1}
\]

where \( e^{RPA}(Z, q) = 1 + 2\pi i \sigma/(Z \text{sgn} Z'' + iq^2D) \) is the disordered RPA dynamical dielectric function, and the diffusion vertex, defined in Fig. 1 a), is

\[
\Gamma(z, Z, q) = \left\{ \begin{array}{ll}
\frac{i/\tau \text{sgn} Z''}{Z+2iqD \text{sgn} Z} \quad z''(z+Z)'' < 0 \\
1 \quad \text{otherwise}
\end{array} \right. \tag{2}
\]

\( D = 1/3 v_F^2 \tau \) and \( '' \) denote the diffusion constant and the imaginary part, respectively, and \( \beta = 1/2 \). The long-range nature of \( v^{eff}_{\vec{q}} \) is a consequence of the hydrodynamic \((Z, q \rightarrow 0)\) pole of \( \Gamma \), Eq. (2). Since diffusion is a classical phenomenon, guaranteed by particle number conservation, the form Eq. (1) of the effective interaction persists at finite \( T \).

There are two experimental indications for the diffusion model of electron transport to be valid in quasicrystals. First, note that the diffusion-enhanced effective Coulomb interaction Eq. (1) implies the well-known \( \sqrt{|E-\varepsilon_F|} \) dependence of the DOS in the pseudogap of disordered systems \[14\], where the half-integer power is characteristic for diffusion. The fact that a powerlaw dip in the DOS at \( \varepsilon_F \) with an exponent very close to \( 1/2 \) has been observed in quasicrystals by tunneling measurements \[13\] may be taken as an indication that the electron motion is indeed diffusive in these systems, and that the effective interaction has indeed the Alt’shuler-Aronov form Eqs. (1), (2). Second, the diffusion model, based on a finite phase coherence length, explains why the spikiness of the DOS, predicted for ideal quasicrystals at \( T = 0 \), has up to now not been observed experimentally \[7\].
3. Electron density response

The incomplete screening of the electron-electron interaction in a diffusive metal may be expected to drastically affect the screening charge distribution around an ion in the electron sea as well. In order to calculate this effect on the Friedel oscillations, we must consider the static charge density response \( \chi(0, q) \) in the vicinity of \( q = 2k_F \). It is given in terms of the polarization function \( \Pi(0, q) \) as \( \chi(0, q) = \Pi(0, q)/(1 - v_F \Pi(0, q)) \). The first term of Fig. 1 b), \( \Pi(0, q) \), corresponds to the well-known Lindhard function (RPA) [18]. In this diagram \( \Gamma \) contributes only a nonsingular factor of \( O(1) \), since here the effective interaction \( v^2_G \) enters in the static limit at wave numbers \( q \approx 2k_F \), where the diffusion vertex \( \Gamma \) is structureless. We are thus led to consider quantum corrections where \( \Gamma \) gives contributions with vanishing frequency and momentum transfer, so that the hydrodynamic transport properties become important, although the response is taken at large external wave numbers \( q \). The most singular contribution of this type arises from the quantum correction \( \Pi(1)(0, q) \), shown in Fig. 1 b), 2nd diagram.

While diffusive density relaxation occurs in general for large times, \( t > \tau \), in \( \Pi(1)(0, q) \) it is, in addition, cut off for times larger than the life time \( \tau_{qp} \) of the quasiparticles, which are interacting via \( v^2_G \). Thus, the frequency transfer in this term extends over the vanishing (see above) range \( \tau_{qp}^{-1} \leq |Z| \leq \tau^{-1} \). It may be evaluated explicitly as [12, 20].

\[
\Pi(1)(0, q) = -C \frac{2m^*k_F \tau_{qp}/\tau - 1}{(2\pi\hbar^2)^2 (\epsilon_F r x)^{3/2}} \times \int_{-\xi_F}^{\xi_F} \frac{d\nu}{1/(4T)} \frac{(x - 1) - \frac{1}{4\sqrt{2\pi} \nu \tau_{qp}}}{(x - 1)^2 + \left(\frac{1}{4\sqrt{2\pi} \nu \tau_{qp}}\right)^2}^{3/4},
\]

where \( x = x(\nu) = (\nu/2k_F)/\sqrt{1 + \nu/\epsilon_F} \) and \( C \) is a numerical constant of \( O(1) \). It is seen that for \( T = 0, \tau_{qp}^{-1} = 0 \) \( \Pi(1)(0, q) \) exhibits a powerlaw divergence \( \propto -\text{sgn}(q - 2k_F)/|q - 2k_F|^{1/2} \) at \( q = 2k_F \). Although at finite \( T \) or \( \tau_{qp}^{-1} \) the divergence of \( \Pi(1)(0, q) \) is reduced to a peak, the inverse dielectric function, \( 1/\epsilon(\nu) = 1/(1 - v_F \Pi(0, q)) \), still has a \( q = 2k_F \) divergence at a critical transport rate, \( \tau_c^{-1}(T) \) because of the vanishing denominator. This leads to a systematical enhancement as well as to a phase shift of the Friedel oscillations (see below). On the other hand, when there is no enhanced backscattering, we have \( \tau_{qp}/\tau = 1 \), and the peak structure of \( \Pi(0, q) \) vanishes. Eq. (3) constitutes an extension of previous work [20] in that the finite quasiparticle life time is explicitly taken into account. The parameter \( \tau^{-1} \) may be varied by changing the composition of the alloy.

\[\text{Fig. 2. Crystallization temperature } T_c \text{ as a function of the DOS suppression at } \epsilon_F, (1 - g). \text{ Data points represent } T_c \text{ for } a-Cu_{1-x}Sn_x \text{ [5]. The solid curve is the fit of the present theory (see text). Vertical line: position of CAT. The inset shows the phase shift } \varphi \text{ of the first maximum of the charge density distribution } \rho(r). \text{ Solid line: theory. Data points with solid line: measurements [5] for } a-Cu_{1-x}Sn_x.\]

4. Comparison with experiments

In the following, the theory developed in the previous section is applied in the region \( 1/\epsilon_F \tau_{qp} \ll 1 \) to a large class of noble-polyvalent metal alloys like \( Cu_{1-x}Sn_x \). These HR alloys exhibit an amorphous to crystalline transformation (CAT) as a function of the composition of the alloy, and the thermal stability may be continuously varied. Remarkably, in all these systems (1) the thermal stability reaches a maximum at or near the CAT (Fig. 2) [3, 4, and 2], assuming that the ions sit in the minima of the Friedel potential, the measured ionic positions suggest that there is a systematical phase shift \( \varphi \) of the Friedel oscillations [3, 4], \( \rho(r) \propto \cos(2k_F r - \varphi) \), with \( \varphi = \pi/2 \) at the CAT (inset of Fig. 2).

Fourier transforming \( 1 - 1/\epsilon(q) \) to obtain \( \rho(r) \) [18] shows that for incomplete Fermi surface-Jones zone matching, i.e. small \( \tau^{-1} \approx \tau_{qp}^{-1} \), the quantum corrections generate density oscillations \( \rho(1)(r) \propto -\cos(2k_F r)/r^3 \), which overcompensate the conventional Friedel oscillations, implying a phase shift of \( \varphi = \pi \) [20]. As \( \tau^{-1} \to \tau_{qp}^{-1} \), the increasing \( 2k_F \) peak of \( 1/\epsilon(q) \) leads, in addition, to density oscillations \( \rho(1)(r) \propto \sin(2k_F r)/r^2 \), so that in the vicinity of \( \tau_{qp}^{-1} \)

\[
\rho(r) \propto -\frac{\cos(2k_F r)}{(2k_F r)^3} + A(\tau_{qp})\frac{\sin(2k_F r)}{(2k_F r)^2},
\]

with \( A(\tau_{qp}) \approx 0.343\pi(1 - \tau^{-1}/\tau_{qp}^{-1})^{-1/2} \). The exponent \( 1/2 \) is characteristic for diffusive behavior.
Thus, the Friedel oscillations are shifted by \( \varphi = \pi - \tan^{-1}(2k_F A(\tau^{-1})) \approx \pi/2 + 1/(2k_F A) \), i.e. the diverging Friedel amplitude necessarily goes hand in hand with \( \varphi \rightarrow \pi/2 + 0 \). Note that, in contrast to the conventional Friedel oscillations, this divergence is robust against damping due to finite \( T \) or disorder. The point where the amplitude, \( A \), diverges should be identified with the CAT, since at this point the fluctuations of the Friedel potential also diverge, allowing the system to find its crystalline ground state. This process explains in a natural way the observed composition dependence of the thermal stability and of the phase shift \( \varphi \) mentioned at the beginning of this section.

For a direct comparison with experiments the control parameter of the theory, \( \tau^{-1} \), must be translated into a parameter which is experimentally accessible: It follows from the scattering theory [19, 20] that \( \tau^{-1} = \tau^{-1}_0 + \gamma S(2k_F) \), where the peak of the ionic structure factor, \( S(q = 2k_F) \), controls the backscattering amplitude, \( \gamma \) is a constant, and \( \tau^{-1}_0 \) is an offset due to momentum independent scattering. \( S(2k_F) \) in turn is proportional to the measured, structure–induced suppression of the DOS \( N(\varepsilon_F) \) at the Fermi level, \( 1 - N(\varepsilon_F)/N_0(\varepsilon_F) \equiv 1 - g \), compared to the free electron gas, \( N_0(\varepsilon_F) \). The resulting fit of the crystallization temperature, \( T_c \), is shown in Fig. 2, where the contribution to the stability coming from the pseudogap formation is assumed to be linear in \( (1 - g) \) (dashed line). The characteristic increase of \( T_c \) at the CAT, explained by the present theory, is clearly seen. The inset shows the calculated phase shift, \( \varphi \), and the measured shift of the atomic nearest neighbor position relative to the position of the first conventional Friedel minimum, \( a_0 = \pi/k_F \). Note that there is no adjustable parameter in \( \varphi \), once the fit of \( T_c \) has been performed. The overall behavior of the shift is well explained by the theory; however, the experimental data approaches \( \varphi = \pi/2 \) faster than predicted. The latter may be attributed to the fact that, as seen from the discussion after Eq. (4), the higher–order Friedel minima approach \( \varphi = \pi/2 \) faster than the first one. In this light, the agreement between theory and experiment is remarkably good.

5. Conclusion

The structural similarities between amorphous alloys and \( i \)-quasicrystals suggest that the quantum effect discussed above may be important in the latter systems as well. In fact, quasicrystals seem to fulfill all the necessary conditions for this effect to occur, i.e. effectively diffusive electron motion [13, 14] and \( \tau^{-1} \gg \tau_{qp}^{-1} \). The latter is supported by the Fermi surface matching, i.e. by the experimental observation [16] and theoretical prediction [5, 17, 18] of structure-induced pseudogaps. Moreover, another more commonly known effect of disorder–enhanced Coulomb interaction, the \( \sqrt{|E - \varepsilon_F|} \) dependence of the DOS in the pseudogap [15], may have been already observed in \( i \)-quasicrystals by tunneling measurements of the DOS [14].

In conclusion, we have shown that the Friedel oscillations are enhanced by Coulomb interaction in the presence of disorder and enhanced backscattering. The results are relevant for the stability of amorphous and quasicrystalline metals. It is proposed to include the enhanced Friedel potential calculated in the present work in the pseudopotential of more quantitative \textit{ab initio} calculations.

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