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## Optical conductivity of icosahedral quasi-crystals

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**Abstract.** It is argued that the optical conductivity of face-centred icosahedral (FCI) quasi-crystals is dominated by band-structure effects. No mechanism peculiar to quasi-periodicity is necessary to explain experiment which is accounted for by semi-phenomenological perturbation theory. What makes FCI quasi-crystals different from conventional metallic alloys is the high multiplicity (namely, 42) of their reciprocal lattice vectors, which allows a better match between the Fermi sphere and the corresponding set of Bragg planes (the 'quasi-Brillouin zone'). This effect is also responsible for a strong reduction in the DC conductivity through a substantial optical mass increase, rather than anomalously strong scattering localization. The low DC conductivity, in turn, means that the weak Drude part of the AC conductivity is overwhelmed by stronger interband absorption, resulting in a suppression of the Drude peak. Otherwise, however, the *interband* absorption peak in an FCI quasicrystal is not significantly different from those in conventional metals.

A notable feature of quasi-crystals (besides the 'forbidden' icosahedral symmetry and six-dimensional geometry used to describe their structure) is their surprisingly low electrical conductivity. While mostly composed of good metals, such as Al, Cu and Fe, quasi-crystals exhibit DC conductivities which can be thousands of times smaller than the conductivity of their constituents [1]. Not only is the conductivity low, but its temperature dependence is also quite unusual for metals: the conductivity *declines* significantly at low temperatures. Further, as the levels of impurity concentration and the structural imperfection are lowered, the conductivity follows suit [2]. The best quality ('defectless') samples of face centred icosahedral (FCI) quasi-crystals, such as  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  and  $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ , have conductivities as low as  $40 \Omega^{-1} \text{cm}^{-1}$  [1, 2] at 4 K (to be compared with approximately  $10^7 \Omega^{-1} \text{cm}^{-1}$  for the pure constituents, and  $10^3 \Omega^{-1} \text{cm}^{-1}$  for a metallic glass of the same composition). Typical conductivities appear to fall far below Mott's minimal metallic conductivity: the mean free path, estimated in a standard manner with a spherical Fermi surface and density of states (DOS) as derived for free electrons, appears to be as low as 1 Å [1]. On the other hand, quasi-crystals are by no means insulators; they might rather be classified as semimetals. Other electronic properties (Hall effect, thermopower, heat capacity [1], optical absorption [3], etc) are also far from usual.

Although the transport properties are not completely understood theoretically, the proposed qualitative explanations fall into two major categories: firstly, wavefunction localization or criticality, and secondly, band structure effects in the Hume-Rothery

picture. The former is based on an assumed inapplicability of the Bloch theorem to the quasi-periodic case, which through associated disorder might open a path to a localization of some kind. In fact, before addressing the transport properties in general it is worth understanding the basic properties of the one-electron spectrum. The major question is this: are eigenfunctions of electrons at a given energy in a quasi-periodic potential localized or extended? To date, the answer is still unknown, except for the one-dimensional case, where wavefunctions are 'critical', i.e. neither localized nor extended [4]. Both outcomes are in principle feasible in two and three dimensions. One cannot exclude the Bloch picture outright solely on the basis of the lack of periodicity; even in a quasi-periodic potential, the eigenfunctions might happen to be extended and if so they can be cast in the familiar Bloch form with the only distinction from the periodic case traced to the fact that the momentum  $k$  cannot be reduced to a single Brillouin zone because of the absence of a *smallest* reciprocal lattice vector. This difficulty is easily avoided by the use of an extended-zone scheme. (A one-dimensional example of such behaviour has been found analytically, long ago [5].) On the other hand, the solution of a quasi-periodic Schrödinger equation might well result in criticality similar to the one-dimensional case, or even in localization. In fact, arguments can be advanced for both criticality [6] and localization [7]. Here we do not address this question directly. Instead we argue that it is not necessary to invoke any of the various localization pictures in order to explain the anomalously low DC conductivities. Instead, the aim of this paper is to explain the experimentally observed DC [1, 2] and AC conductivities [3] within the framework of the alternative 'band-structure hypothesis' [1, 8, 10].

The band-structure approach does not address the quasi-periodic Schrödinger equation at all; the existence of a quasi-momentum  $k$  is taken for granted (i.e. there is no localization, at least near the Fermi surface). In this approach, anomalously low conductivity is attributed, not to a short mean free path, but to an extremely low DOS at the Fermi level (as in semimetals). The low DOS, in turn, is believed to be a consequence of the Hume-Rothery electronic stabilization mechanism [1, 8–10], which implies a close contact of the Fermi surface with several Bragg planes, whose associated reciprocal lattice vectors  $G$  satisfy  $2k_F \approx G$ , where  $k_F$  is the Fermi wavevector. Interaction with the Bragg planes results in the opening of pseudo-gaps and then to a related reduction in energy. There is experimental and theoretical evidence that gives partial support to this scenario, but it is not completely convincing. The first is a strong dependence of conductivity on the alloy composition, as reported in [1, 2]. The proposed pseudo-gaps are rather narrow, but the DOS at the minimum is also quite low, from which it follows that the slope of DOS is steep (figure 1). Accordingly, even small variations in composition, which shift  $E_F$ , can cause large changes in the DOS and the conductivity. There is direct evidence of a low DOS; both specific heat measurements [1] and soft-x-ray emission and photoabsorption experiments [11] reveal very small values. Theoretical efforts also tend to support the hypothesis, including fairly realistic band-structure calculations for specific alloys [10, 12, 13, 26]. However, such calculations are complicated by three significant obstacles.

Firstly, existing computer algorithms rely on periodicity.

Secondly, the actual atomic structures of quasi-crystals are still largely unknown.

Thirdly, the best quasi-crystals contain transition metal atoms with complexities arising from d bands near the Fermi energy.

For these reasons calculations have generally been made on periodic approximants

of FCI quasi-crystals. The calculations [12, 13, 26] tend to show a prominent pseudo-gap near the Fermi surface and a strongly suppressed DOS. Unfortunately, even low-order 1/1, 1/2 approximants still contain several hundred atoms in a unit cell which makes direct band-structure calculations numerically intensive. Not surprisingly, the calculation of properties (e.g. optical absorption) even for low-order approximants shares the same difficulty. Fortunately, it appears that these direct methods can be avoided. The existing experimental optical data [3, 27] are at least partly explicable by *perturbation theory with the use of nearly free electrons* in an effective-mass framework. This constitutes the second claim of the present paper: we suggest that wavefunctions (at least not too far from  $E_F$ ) are not merely extended but are also representable as linear combinations of a small number of plane waves, mixed by a quasi-periodic pseudopotential. This interesting property was first noticed in direct numerical calculations [12] and has been confirmed recently in similar band-structure calculations [13] (the latter being carried out on impressive 5/3 approximant of 12000 atoms/cell). The role of d electrons, which are clearly important in the understanding of the pure transition metal constituents is not completely clear. Experiment [11] and band-structure calculation [26] both indicate the presence of d band peaks in the DOS, but they are at 6 eV (Cu) and 2 eV (Fe) below the Fermi energy. The presence of some d character at the Fermi level cannot be excluded [26], however, we shall assume that d electron effects do not seriously affect the transport and optical properties.

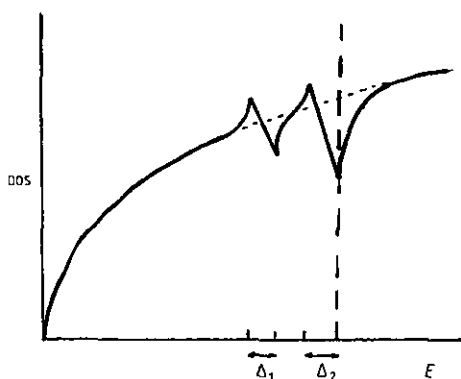


Figure 1. DOS versus energy (the pseudo-gaps do not overlap): ---- preferred position of the Fermi level.

It should be emphasized that the present work is not a band-structure calculation *per se*; we do not attempt to calculate the spectrum from first principles (as is done in [12,13,26]), but we presume that there are some pseudo-gaps near the Fermi energy. Our intent is to relate their widths and positions to the optical conductivity  $\sigma(\omega)$ , which is reported in [3]. The evident agreement with experiment appears to be reasonable corroboration that a simple perturbation theory approach is meaningful.

To begin with we must justify the claim made that  $2k_F$  is of order  $G$ , a reciprocal lattice vector. This will be done in two ways, with the same results. The first method is direct: we apply the conductivity sum rule

$$\int \sigma(\omega) d\omega = \frac{\omega_p^2}{8} \quad \left( \omega_p^2 = \frac{4\pi n_e e^2}{m} \right) \quad (1)$$

to the experimentally measured  $\sigma(\omega)$  [3]. From this we obtain a plasma frequency  $\omega_p$  equivalent to 12.7 eV and a corresponding  $n_e = 1.2 \times 10^{23}$  electrons  $\text{cm}^{-3}$  and, hence, a Fermi wavevector  $k_F = (3\pi^2 n_e)^{1/3} = 1.52 \text{ \AA}^{-1}$ . The second argument stems from an extensive study of stability of different FCI quasi-crystals [14]; the major claim of this study is that all FCI quasi-crystals, independent of their chemical composition, are most stable at 1.75 electrons/atom and when the Cu content is twice the transition-metal content. Tsai *et al* [14] used a negative effective valence of the transition metal, e.g.  $-2.85$  for Fe in the well known quasi-crystal  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ , which we are going to deal with below. (We believe that a similar mechanism with slightly different values of parameters applies to other stable FCI quasi-crystals.) An interesting explanation of this long-standing negative effective valence hypothesis, based on a generalized impurity Hubbard model, has recently been given [26]. Multiplying the above *average* valence  $Z = 1.75$  by the number of atoms  $n_a$  per unit volume, we obtain an electron density  $n_e = Zn_a$ . The number density  $n_a$  is, in turn, derived from the experimentally measured mass density of  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  of  $4.5 \text{ g cm}^{-2}$  [15]. This gives  $n_e = 1.2 \times 10^{23} \text{ e cm}^{-3}$  and  $2k_F = 3.05 \text{ \AA}^{-1}$ , in agreement with the direct method. We may notice that this value is very close to the positions of two strongest peaks in the  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  diffraction pattern:  $G_1 = (4, 2, 2, 2, 2, 2) = 2.98 \text{ \AA}^{-1}$  and  $G_2 = (4, 4, 2, 0, 0, 2) = 3.13 \text{ \AA}^{-1}$ . The first peak is in five-fold direction and has multiplicity 12; the second peak is in the two-fold direction, with multiplicity 30 [16]. Accordingly, the (originally spherical) Fermi surface is most influenced by the 42 closest and 'strongest' Bragg planes. Note that, although reciprocal lattice vectors are known to fill the space everywhere densely, thereby creating a *dense set* of Bragg planes, not all of them are of physical importance. Components of the pseudopotential  $V_G$  decrease rapidly with increase in the magnitudes of the six-dimensional reciprocal lattice vectors  $G$ , and for this reason only a few strongest components are of physical significance. The others (the majority) are weak and can be neglected (see [8]). Since  $V_G$  is proportional to the geometric structure factor  $S_G$ , only those  $G$ -values that are prominent in the diffraction pattern can contribute substantial  $V_G$ ; the Bragg planes associated with faint diffraction peaks are of far less importance. For these reasons we neglect all the Bragg planes except the strongest, which number 42 in all. For each Bragg plane in this group the electron energy in its vicinity is given by

$$E(k) = E^{(0)}(k) + \frac{1}{2}\Delta \left( \gamma \pm \sqrt{1 + \gamma^2} \right) \quad \gamma = (8E_0/\Delta)[(k_{\parallel} - G/2)/G] \quad (2)$$

where  $\Delta = 2V_G$  is the width of the corresponding pseudo-gap,  $E_0 = E^{(0)}(G/2)$  and  $k_{\parallel}$  is a component of  $k$  in the  $G$  direction. We assume that the gaps  $\Delta_1$  and  $\Delta_2$ , associated with  $G_1$  and  $G_2$ , respectively, are small enough so that regions of  $k$ -space, where corrections (2) to the free electron spectrum  $E^{(0)}(k)$  are substantial, do not overlap; contributions from the 42 Bragg planes are then additive. This proposition does not mean that the pseudo-gaps  $\Delta_1$  and  $\Delta_2$  do not overlap on the  $E$ -axis; they might do so or not, depending on the relative values of  $\Delta_1$  and  $\Delta_2$  and their positions (figure 1). The additivity (i.e. linearity) assumption simply means that the flat regions on the Fermi surface (figure 2) do not overlap. The particular shape of the Fermi surface depends on  $E_F$  and the pseudo-gap parameters; figure 2 sketches the situation for the case where  $E_F$  lies inside the upper pseudo-gap (associated with  $G_2 = 3.13 \text{ \AA}^{-1}$ ). In what follows the actual Fermi level is treated as an adjustable parameter, because it is a function of the alloy composition. It is

only required by the Hume-Rothery rule to be somewhere near the pseudo-gap [8–10]. The strongest suppression of the DC conductivity is reached when  $E_F$  coincides with the DOS minimum, i.e. the upper edge of the second pseudo-gap. This position is also favourable from the Hume-Rothery point of view and for these reasons we will often use  $E_F = E^{(0)}(G_2/2) + \Delta_2/2$  as a preferred value. Because of thermal expansion the pseudo-gaps will be functions of temperature and, since much of the Fermi surface is obliterated, this is not necessarily a small effect (and may well be involved in the *increase* in conductivity with increasing temperature).

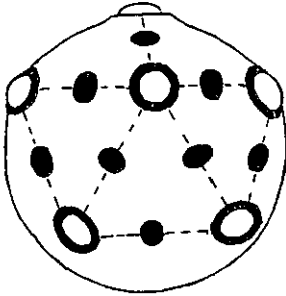


Figure 2. Proposed Fermi surface of a FCC quasi-crystal (extended-zone scheme). Ring-like flat spots are associated with the lower pseudo-gap  $\Delta_1$  and circular spots with  $\Delta_2$ . If the reduced zone scheme were applicable, the caps on the ring-like flat spots would be in the second Brillouin zone.

The situation that we have arrived at is rather similar to one in, say, Al or indeed an alloy of nearly free electron metals. When dealing with one particular Bragg plane nothing specifically quasi-crystalline emerges; we do not rely on quasi-periodicity itself. What makes the electronic properties of quasi-crystals quite distinct from those of crystals is the icosahedral symmetry of the former. We argue that each individual flat region on the Fermi surface is not significantly larger than might be found in an alloy of free electron metals and can be treated in the same manner, but here there are 42 such regions and the key issue is the high multiplicity of icosahedral reciprocal lattice vectors. This statement is supported by the recently observed resemblance of the transport properties of crystalline and quasi-crystalline modifications of AlMnSi [17, 27]. The DC conductivity of  $\alpha$ -AlMnSi, a low-order rational approximant of icosahedral AlMnSi, is as low as it is in quasi-crystalline  $\tau$ -phase. Furthermore, exactly as for the quasi-crystals, the DC conductivity *decreases* in better-quality samples [17], and for both the optical properties are actually quite similar [27]. The approximant phase is undoubtedly periodic, and localization mechanisms specific to quasi-periodicity should therefore not apply but, on the other hand, its structure is almost icosahedrally symmetric, and this therefore opens a path to Fermi surface—Bragg plane interaction mechanism as described above. The deviation from the icosahedral symmetry in  $\alpha$ -AlMnSi is rather small and the Bragg planes are located in positions very close to those of the icosahedral phase, permitting effective contact with the Fermi sphere.

Accordingly, we treat the effect of a single small pseudo-gap on DC and AC conductivities in the same manner as in conventional crystalline polyvalent metals. The latter problem was solved 20 years ago by Ashcroft and Sturm [18] who employed perturbation theory. Here we mainly apply the results of that work to a new substance, but with extended calculations performed in the spirit of [18].

The DC conductivity can be written as

$$\sigma = \frac{1}{3} e^2 \tau \frac{1}{4\pi^3 \hbar} \int_{\text{FS}} v \, dS = \sigma^{(0)} - \sum_{j=1}^{42} \delta\sigma_j \quad (3)$$

where  $\tau$  is a relaxation time, the integral is taken over the Fermi surface,  $\sigma^{(0)}$  is an unperturbed free electron value of  $\sigma$  and  $\delta\sigma_j$  are corrections from 42 (independent) flat regions on the Fermi surface. Before proceeding, it is important to note that the flat regions are actually excluded from the integral in equation (3). (In the familiar reduced-zone scheme they do not exist at all.) So, the larger the flat regions, the lower is the conductivity. A very crude approximation then suggests that

$$\sigma \approx \sigma^{(0)} (S_{\text{F}}^{(0)} - S_{\text{flat}}) / S_{\text{F}}^{(0)}. \quad (4)$$

However, the Fermi velocity is not constant on the Fermi surface and more accurate calculations are needed. A single term in equation (3) is calculated by the method in section V of [18] to give

$$\delta\sigma = \frac{\sigma_a}{2b} \int_1^\infty \frac{s(w) \, dw}{w^2 \sqrt{w^2 - 1}} \quad (5)$$

where

$$\sigma_a = (1/6\pi^2)(e^2 G/\hbar) \sim 1200 \, (\Omega \text{ cm})^{-1} \quad b = \hbar/\tau\Delta \quad w = \sqrt{1 + \gamma^2} \quad (6)$$

$$s(w) = \begin{cases} w & 1 < w < w_0 \\ \frac{1}{2}[w_0 + w - (w^2 - 1)/8\epsilon_0] & w > w_0 \end{cases} \quad (7)$$

$$\epsilon_0 = E_0/\Delta \quad \epsilon_{\text{F}} = E_{\text{F}}/\Delta \quad w_0 = 2(\epsilon_{\text{F}} - \epsilon_0).$$

It is seen from equations (2) and (6) that  $w$  is simply a dimensionless splitting between the upper and lower branches of the perturbed spectrum in the vicinity of a Bragg plane and  $s(w)$  is a dimensionless area of the Fermi surface cross section, which consists of points  $k$  such that  $E(k) < E_{\text{F}}$  and  $E(k + G) > E_{\text{F}}$ ; it is introduced to represent the integrals over the three-dimensional  $k$ -space as integrals over  $k_{\parallel}$  and  $k_{\perp}$  [18]. Note that  $s(1)$  is the area of the flat region on the Fermi surface.

Integral (5) is straightforward to calculate: we obtain

$$\delta\sigma = \begin{cases} (\sigma_a/4b)(\pi/2 + w_0) & w_0 < 1 \\ (\sigma_a/4b) \left[ \pi/2 + w_0 + \tan^{-1} \left( \sqrt{w_0^2 - 1} \right) - \sqrt{w_0^2 - 1} \right] & w_0 > 1 \end{cases} \quad (8)$$

(where terms containing  $1/8\epsilon_0 \approx \Delta/8E_{\text{F}} \ll 1$  are neglected). The expressions in parentheses, although parameter dependent, are of the order of 1 and do not affect the magnitude of the final result; accordingly,

$$\sigma \simeq \sigma^{(0)} - 42C\sigma_a/4b \quad C \simeq 1. \quad (9)$$

Here  $\sigma^{(0)}$  and the correction  $\delta\sigma$  take the forms

$$\sigma^{(0)} = (1/6\pi^2)(e^2 2k_{\text{F}}/\hbar)(2E_{\text{F}}/\hbar)\tau \quad \delta\sigma = (1/6\pi^2)(e^2 G/\hbar)42(C/4)(\Delta/\hbar)\tau. \quad (10)$$

If we estimate  $E_F \sim 9$  eV, we can easily see that a pseudo-gap  $\Delta$  of about 0.5 eV is enough to reduce the conductivity to virtually zero. Once again, the key issue in this picture is the factor of 42, arising from the high multiplicity of icosahedral diffraction peaks, which enhances the correction  $\delta\sigma$  in equation (10). The crude estimate that we present here surely cannot be used for very low conductivities because, when the correction becomes almost equal to the original value of  $\sigma$ , our assumption of flat-area additivity is no longer valid. However, equation (10) clearly shows that even reasonably small pseudo-gaps (of about 0.5 eV or, in other words,  $\frac{1}{20}E_F$ ) are sufficient to make almost the entire Fermi surface flat, reducing the conductivity to a very small value. Note that pseudo-gaps were found in [11–13] to be about 1 eV; so our 0.5 eV values do not look too large. More accurate results are obtained by using equations (3) and (7) with two different pseudo-gaps  $\Delta_1$  and  $\Delta_2$ . The use of different parameters and smaller  $\Delta$ -values (of about 0.3 eV), which still allow us to stay in the linear range, however, give results similar to the estimates of equations (9) and (10); the conductivity can be very strongly reduced, down to approximately  $500 \Omega^{-1} \text{ cm}^{-1}$ , which is just the value found in [3].

The DOS is obtained in a standard manner within the same perturbation approach (2). The result depends on parameters, and a reasonable possibility is shown in figure 1. A rough idea of the orders of magnitudes can be obtained by estimating the minimal value of the DOS  $\nu$  from

$$\nu \sim \nu^{(0)}(1 - 42\Delta/8E_F). \quad (11)$$

Substituting  $\Delta \sim 0.5$  eV, which, according to equation (10), reduces the conductivity to almost zero, gives a rather moderate DOS reduction of about 33%. (An even larger reduction of about 60% was given in [1, 11–13].) Although our estimate (11) is quite approximate, it explains an old paradox: according to [1, 11–13] the DOS is reduced by a factor of 3 only, whereas the conductivity is changed by a factor of 100 or even more [1]. The simple formula usually used for DC conductivity is

$$\sigma = \frac{1}{3}e^2 v_F^2 \nu_F \tau \quad (12)$$

but it is, in fact, a particular case, derived from a more general expression (3) provided that the Fermi surface is spherical and  $v_F$  is constant. In FCI quasi-crystals this is certainly not the case; the Fermi surface is far from spherical (figure 2) and  $v_F$  is also by no means constant. Further, not only is the DOS  $\nu_F$  small, the Fermi velocity  $v_F$  is also small. So, the oversimplified formula (12) does not apply to this case; the use of the more accurate expressions (9) and (11) shows that the reduction in the conductivity is not merely proportional to the DOS.

The AC (optical) conductivity is, as usual, a sum of an intraband (Drude) term

$$\sigma_D(\omega) = \sigma_0/[1 + (\omega\tau)^2] \quad (13)$$

(where  $\sigma_0$  is the DC conductivity; see above), and an interband term, calculated by making use of the Kubo formula (equation (14) of [18])

$$\begin{aligned} \sigma_{IB}(\omega) = & \frac{e^2 \hbar}{3m^2 i \omega V} \sum_{\mathbf{k}} \frac{|M(\mathbf{k})|^2 (\hbar\omega)^2}{[(E_+(\mathbf{k}) - E_-(\mathbf{k}))^2]} \\ & \times \left( \frac{1}{E_+(\mathbf{k}) - E_-(\mathbf{k}) - \hbar(\omega + i/\tau)} + \frac{1}{E_+(\mathbf{k}) - E_-(\mathbf{k}) - \hbar(\omega + i/\tau)} \right) \end{aligned} \quad (14)$$



where  $M(\mathbf{k}) = \langle \psi_+(\mathbf{k}) | \nabla | \psi_-(\mathbf{k}) \rangle$ , the  $E(\mathbf{k})$  are given by equation (2) and  $\tau$  is a phenomenological relaxation time. This interband  $\tau$  can differ from the relaxation time appearing in the Drude part, but usually the difference is not too large [18]. (The generalization for two different  $\tau$ -values is obvious.) The introduction of a relaxation time  $\tau$  into equation (14) is a physical necessity. In FCI quasi-crystals, as in Al [18], parallel bands are present (figure 3). Their occurrence makes the situation similar to the one-dimensional case: in the absence of scattering the conductivity at the absorption edge *diverges* [18]. For this reason the magnitude of the interband maximum displays both strong  $\tau$  and temperature dependences [20].

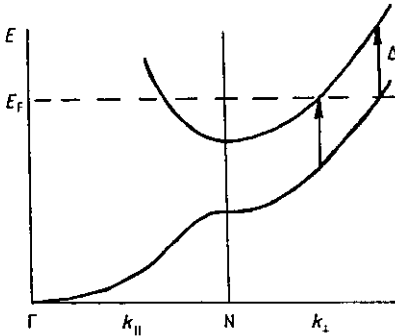


Figure 3. Parallel bands.

The contribution to  $\sigma_{\text{IB}}(\omega)$  from a single Bragg plane differs little from the corresponding contribution in Al [18], namely

$$\sigma = \sigma_a b z^2 \int_1^\infty \frac{1}{w^4 + 2(b^2 - z^2)w^2 + (b^2 + z^2)^2} \frac{s(w)dw}{w^2 \sqrt{w^2 - 1}} \quad (15)$$

where  $z = \hbar\omega/\Delta$  is a dimensionless frequency, and the other variables are defined in equations (6) and (7). The total  $\sigma_{\text{IB}}(\omega)$  is simply the sum of contributions from 12 pseudo-gaps  $\Delta_1$  and 30 pseudo-gaps  $\Delta_2$ . The integral (15) can be given in closed form and is given in [18]. Figure 4 gives a better idea of what it is. In the case of  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  the theoretical result (15) fits the experiment [3] quite well with  $\Delta \sim 0.5$  eV and  $\tau \sim 0.5 \times 10^{-15}$  s, which gives the value of  $b = \hbar/\tau\Delta \sim 3$ . The  $b \gg 1$ , and  $w_0 \gg 1$  limits of equations (15) are quite simple, namely

$$\sigma(\omega) = \sigma_a (\pi/2) (\Delta/\hbar\tau) \{(\omega\tau)^2 / [1 + (\omega\tau)^2]^2\}. \quad (16)$$

We can see in figure 4 that even this limiting form agrees with the experiment quite well; the best fit is achieved with  $\Delta = 0.45$  eV, and  $\tau = 0.47 \times 10^{-15}$  s ( $\Gamma = \hbar/\tau = 1.4$  eV). Equation (16) contains only two parameters namely  $\Delta$  and  $\tau$  ( $\sigma_a \sim 1200 \Omega^{-1} \text{cm}^{-1}$  is a constant; see equation (6)). The function has a maximum at  $\omega = 1/\tau$ , for which  $\sigma_{\text{max}} = \sigma_a (\pi/8) (\Delta/\hbar)\tau$ . (After  $\Delta$  and  $\tau$  have been obtained by fitting the position of the maximum, there are no further parameters to adjust; nevertheless the agreement remains good.) Note that the value of  $\Delta \sim 0.5$  eV is in remarkable agreement with the estimate (10) obtained from the DC conductivity. It is also worth mentioning that in the case  $b = \Gamma/\Delta \gg 1$  the interband peak occurs at  $\hbar\omega = \Gamma = \hbar/\tau$ , and not at  $\hbar\omega \sim \Delta$ , as is usually the case.

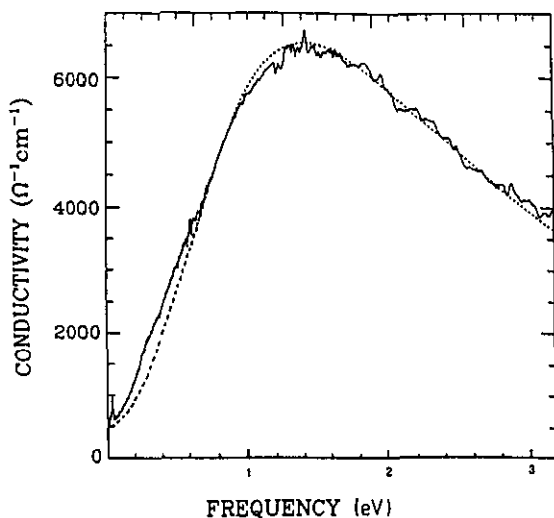


Figure 4. Conductivity  $\sigma(\omega)$  of  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ : ---- fit with equation (16).

The phenomenological relaxation time of  $\tau \simeq 0.5 \times 10^{-15}$  s obtained above by fitting the optical data [3] with equation (16) is rather short; it is about eight times shorter than in pure Al. Although we do not yet know the precise origin of such strong scattering, we may suggest certain mechanisms. First, it should be noted that there are two factors cutting off the parallel band divergence: scattering, phenomenologically described by  $\tau$ , and deviation from parallelism. As discussed in [19] the latter is not a trivially small effect, but can nevertheless be roughly described by introducing corrections to the approximate formula (2). Such corrections could also include mixing of more than two plane waves, energy dependence in pseudopotentials, etc. In any event, the bands are no longer parallel and the peak intensity becomes finite *even without scattering*. The combined effect of both non-parallelism and scattering is even more pronounced. Sometimes it is not easy to separate these two effects, and a certain fraction of the fitted phenomenological  $\tau$  might originate not from scattering at all but from non-parallelism [19]. In this case the true scattering time  $\tau$  is longer than the fitted value of  $0.5 \times 10^{-15}$  s. Another possible reason for stronger scattering than in Al is the complexity of the alloy. For example chemical disorder is reported in  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ ; there are positions where Cu and Fe are randomly mixed [21]. Disorder of this type is well known to be responsible for rather large residual conductivities in regular alloys. Other structural disorder could be present in the samples studied in [3], and they are known to exhibit a great deal of diffuse scattering in their diffraction patterns. Electron-phonon interactions can also be a source of scattering and in quasi-crystals such processes can be enhanced by a plurality of *Umklapp* processes (recall that reciprocal lattice vectors fill the space everywhere densely!). The presence of a d band about 2 eV below  $E_F$  [11, 26] can also contribute to the finite lifetime of our 'free' electrons. The assumption being made is that in spite of these short lifetimes the essential metallic character of the system implies that at least in the neighbourhood of the Fermi energy the wavevector  $k$  can be taken as a reasonably good quantum number. It might happen that at some other energies there are localized (critical) states which are not characterized by any  $k$ -vector at all. Since our plane waves are not exact eigenstates, they might have non-zero overlap with such hypothetical 'localized' states. This mechanism is somewhat analogous to

a conventional scattering from structural defects. In the latter case the plane waves interact with states localized by a random impurity potential; in the quasi-crystalline case the states might be localized by the quasi-periodic crystal potential itself. In any case, some localization phenomenon originating either from quasi-periodicity or from conventional randomness have been reported in FCI quasi-crystals [1, 22].

Although  $\tau$  appears to be short in one sense, in another it is quite normal for alloys. For example, the relaxation time in brass, which lacks the complexity of  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  but does possess chemical disorder, is  $1.1 \times 10^{-15}$  s [24], which is only 2.5 times larger than in  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ . Another pertinent system with which to compare is the conventional alloy  $\text{Li}_{1-x}\text{Mg}_x$ , a BCC solid solution over much of the range of  $x$ . The interband absorption is dominated by the intersection of the Fermi surface with only 12 Bragg planes. The Fermi wavevector  $k_F$  increases smoothly with increasing Mg content, providing a series of  $\sigma(\omega)$  curves [24], which can be described in interband terms by equation (15). A typical interband relaxation time  $\tau$  is  $3 \times 10^{-15}$  s (the corresponding Drude value of  $\tau$  is  $1.2 \times 10^{-15}$  s) and these times show relatively little concentration dependence in the BCC region. In this system,  $\sigma_0$  is not particularly low (almost  $5000 \Omega^{-1} \text{cm}^{-1}$ ); it corresponds to a total flat area on the Fermi surface of about 20%. The difference between  $\tau$  for LiMg and  $\tau$  for  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  of a factor of 6 is not unreasonable, especially because residual conductivities of alloys are known to vary by factors of 10–100 upon relatively slight changes in alloy composition. In any event the  $\tau$ -value of about  $0.5 \times 10^{-15}$  s proposed here does not look implausible. However, there remains the question of applicability of the nearly-free-electron approach, which in  $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$  appears to be valid. Indeed, we estimate the Fermi momentum to be about  $1.5 \text{ \AA}^{-1}$ , the Fermi energy  $E_F$  to be about 9 eV, the pseudo-gap  $\Delta$  to be about 0.5 eV, the relaxation time  $\tau$  to be about  $0.5 \times 10^{-15}$  s and the damping constant  $\Gamma = \hbar\tau$  to be about 1.4 eV. We see that although  $\Gamma$  is three times the pseudo-gaps  $\Delta$ , it is still only a sixth of  $E_F$ , which supports the use of the Kubo formula (14) and the nearly-free-electron approach. Note that, if there were no band-structure effects at all, the condition  $E_F\Gamma \gg 1$  would be equivalent to the more familiar  $k_F l \gg 1$ . In the present case it is not quite obvious what the mean free path  $l = v_F\tau$  means, because  $v_F$  is far from being constant on the Fermi surface; it even vanishes at some points. Depending on how one defines the average over the Fermi surface the mean free path varies from 2 to 8 Å; as a consequence,  $k_F l$  is estimated as being between 3 and 12, which is still on the metallic side of Mott's criterion. Estimates of mean free paths have recently been made in a phenomenological manner by making use of different experimentally determined quantities such as the DC conductivities and densities of states as determined from specific heat measurements [25]. The results are in essential agreement with our value with  $l$  falling into the 3–6 Å range.

One of the most surprising features of  $\sigma(\omega)$  measured in [3] is the unusual low-frequency behaviour; the Drude peak appears to be absent and  $\sigma(\omega)$  seems to be increasing linearly with increasing  $\omega$ . With respect to the apparent absence of the Drude peak, the explanation is rather simple; the Drude contribution (13) is actually *not* entirely absent. Rather,  $\sigma_0$ , the DC conductivity, is so small that the Drude term (13) is simply overwhelmed by the large interband term. This explanation is quite general and clearly goes beyond the range of applicability of the perturbation theory adopted here. Indeed, if one adds to the conventional Drude term (13) a rapidly increasing interband term, the total  $\sigma(\omega)$  behaves in the following manner: if  $\sigma_0$  is sufficiently large (as is the case in conventional metals), then  $\sigma(\omega)$  indeed has a

maximum at  $\omega = 0$ ; however, if  $\sigma_0$  is sufficiently small, the maximum disappears and the total  $\sigma(\omega)$  increases monotonically (figure 4). This is a combination of trivial mathematics and the observation, first made in [18], that, in the presence of scattering,  $\sigma_{\text{IB}}(\omega)$  does not vanish even at  $\omega < \Delta$ . The linear behaviour of  $\sigma(\omega)$  reported in [3] is a more subtle issue. Our theoretical curve for  $\sigma(\omega)$  (figure 4) explains quite well the position of the maximum, and the shape of the curve near it and at large  $\omega$ , but, it does not exhibit linear behaviour at very small  $\omega$  (instead,  $\sigma(\omega) = \sigma_0 + \text{constant } \omega^2$ ). This discrepancy with experiment is not surprising at all, taking into account the extreme simplicity of the model used. Introducing corrections to either the spectrum  $E(k)$  (equation (2)) or to matrix elements  $M(k)$  in equation (14) might well modify the result. Also, the very phenomenological approach (14) based on a unique constant  $\tau$  might cease to be valid at very small  $\omega$ . On the other hand, the actual  $\sigma(\omega)$  might also not be linear down to zero  $\omega$ . Indeed, if there is no singularity at  $\omega = 0$ , analyticity requires  $\sigma(\omega)$  to switch from linear to quadratic behaviour at sufficiently small  $\omega$ . This is precisely what our theoretical curve (16) does reveal: it looks rather linear at moderate  $\omega$ , turning to  $\omega^2$  at smaller values. Such 'pseudolinear' behaviour on the left shoulder of interband peaks occurs in other materials which have absolutely nothing to do with quasi-periodicity. What again makes quasi-crystals 'special' is the *apparent* absence of the Drude peak at  $\omega = 0$ . Our simple model explains this fact as well as the shape, magnitude and the position of the interband absorption maximum. However, a more accurate approach is certainly needed to investigate the low- $\omega$  limit. It might well include a band-structure calculation that mixes more than two plane waves. The other possible phenomenon which might be responsible for linear  $\sigma(\omega)$  at low  $\omega$  is touching or overlapping of flat regions, i.e. the existence of points on the Fermi surface where the pseudo-gap is zero (cf pure Al, [28]). This is the subject of the further study.

## Conclusion

The semi-phenomenological theory developed here qualitatively explains the sharp decrease in DC conductivity observed in quasi-crystals as well as more moderate suppression of the DOS at the Fermi level. It explains the *apparent* disappearance of the Drude peak in optical conductivity and quantitatively accounts for the interband absorption peak. Quasi-periodicity is never explicitly used in the course of calculations. Accordingly, the results can be equally well applied to periodic approximants of the same alloys. The theory very much relies on the icosahedral symmetry to the extent that it is manifested in the Fermi sphere–Bragg plane interactions, as dictated by the Hume-Rothery viewpoint. In this respect the consequent agreement with experiment appears to favour the band-structure hypothesis over quasi-periodic criticality or localization.

A short communication of the main results will appear in [29].

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