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Quantum diffusion of electrons in quasiperiodic and periodic approximant lattices in the rare earth-cadmium system

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ABSTRACT

Icosahedral quasicrystals are characterised by the absence of a distinct Drude peak in their low-frequency optical conductivity and the same is true of their crystalline approximants. We have measured the optical conductivity of *i*-$GdCd_{7.98}$, an icosahedral quasicrystal, and two approximants, $GdCd_6$ and YCd_6. We find that there is a significant difference in the optical properties of these compounds. The approximants have a zero frequency peak, characteristic of a metal, whereas the quasicrystal has a striking minimum. This is the first example where the transport properties of a quasicrystal and its approximant differ in such a fundamental way. Using a generalised Drude model introduced by Mayou, we find that our data are well described by this model. It implies that the quantum diffusion of electron wave packets through the periodic and quasiperiodic lattices is responsible for these dramatic differences: in the approximants, the transport is superdiffusive, whereas the quasicrystals show subdiffusive motion of the electrons.

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1. Introduction

Quasicrystals are a class of crystals that, rather than possessing periodic translational symmetry of the lattice, have a quasiperiodic order that still gives rise to a discrete diffraction pattern [1]. Despite being discovered three decades ago, we still cannot calculate the band structures of quasicrystals without resorting to approximations to periodic crystals. Consequently, we cannot accurately predict their transport properties, since the powerful Bloch theorem does not apply. This makes it necessary to experimentally compare quasicrystals to their periodic analogues: quasicrystal approximants.

With their large unit cells, similar stoichiometries, similar atomic clusters and diffraction patterns with pseudo-forbidden symmetries, approximants are the closest things to quasicrystals without quasiperiodic lattices [2]. This similarity allows experimentalists to explore the physics unique to the quasiperiodic lattice by looking for the differences between quasicrystals and their approximants.

In previous works [3–10], icosahedral quasicrystals and their approximants showed broad interband transition (IBT) maxima around 1-3 eV with optical conductivities

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between 1600 to 13000 (Ω cm)$^{-1}$. At low photon energies, there is what appears to be either a highly suppressed Drude peak or the absence of a Drude peak altogether. The samples of RMgZn (R=Y, Ho, Er), with the most prominent so-called Drude peak, are not compared to approximants and have a DC conductivity of around 6000 (Ω cm)$^{-1}$ with an IBT maxima around 8000 (Ω cm)$^{-1}$ [10].

In the instances that authors compared icosahedral quasicrystal to their approximants [7,9], the approximants had quite similar optical conductivities to the quasicrystals. Due to this similarity, it has been concluded that the quasiperiodic lattice was not the cause of the peculiar optical conductivities [9]. It should be noted that one of the samples of Demange et al. [4] use a significantly different definition of an approximant that would accept γ-AlCrFe as both a decagonal and icosahedral approximant. Demange et al. admit it is a poor approximant because of the anisotropy and small lattice constants. We simply consider it a poor metal and ignore it here.

Recent results suggest that magnetic properties can manifest differently in quasicrystals and their approximants [11,12]. There are further hints that transport properties are also affected by quasilattices; in the Au–Al–Yb system, DC resistivity measurements as a function of temperature show differences between periodic and quasiperiodic lattices; however, these effects are small and at low temperature (see Figure S1(a) in Deguchi et al. [12]).

Inspired by the linear optical conductivity of aluminium-based icosahedral quasicrystals and their approximants, Mayou [13] derived a generalised Drude model (GDM) to account for the quantum diffusion of electron waves that spread, in time t, according to

$$L(t) = \sqrt{\left\langle [X(t) - X(0)]^2 \right\rangle} \propto t^{\frac{\alpha+1}{2}}, \tag{1}$$

where $X(t)$ is the position operator of the wave packet and α is restricted to $-1 \leq \alpha \leq 1$. In a classical picture, $L(t)$ could be regarded as the square root of the mean square displacement of a macroscopic particle. However, in this model, transport is an inherently quantum phenomenon because the semiclassical Bloch–Boltzmann picture does not always apply, as it requires that the average distance a wave packet travels be greater than the spread of the wave packet itself. However, $L(t)$ is still a measure of the displacement of the wave packet from its initial position. At precisely $\alpha = 0$, the spreading is called diffusive and is analogous to classical Brownian motion. For $\alpha \geq 0$ and $\alpha \leq 0$, we are in the superdiffusive and subdiffusive regimes, respectively. When $\alpha = 1$ we recover the classical Drude model in Equation (2).

Mayou proposed a generalised Drude model of the form:

$$\sigma(\omega) \approx e^2 n(\mu) A \Gamma(\alpha + 2) \left(\frac{\tau}{1 - i\omega\tau} \right)^{\alpha} \tag{2}$$

where $n(\mu)$ is the density of states at the chemical potential, A is a constant, Γ is the gamma function, ω is the frequency, τ is the mean time between scattering and α characterises the quantum diffusion of the wave packet and takes the values $-1 \leq \alpha \leq 1$. In this model, when the electrons are travelling superdiffusively, there is a peak at zero frequency in the conductivity that decreases monotonically with photon energy, like the Drude model.

When travelling subdiffusively, the electrons will have a dip in their conductivity at zero frequency that increases monotonically with photon energy (see Figure 1 in [14]).

There have been many other methods of modelling the optical conductivities of quasicrystals. Deigiorgi et al. [5] and Bianchi et al. [8] conduct a standard analysis using Drude and Lorentz oscillators. Basov et al. [7] fit the interband transitions to a simple bandgap model. The GDM has been used once before by Demange et al. [4], but the low-frequency fit did not account for the low-frequency tails of interband transitions. Burkov et al. [14] interpret the linear conductivity in terms of an admittedly simple, nearly free electron model that uses high-intensity Bragg peaks to define a Jones zone. Wu et al. [9] use the Burkov model plus a Drude component. Karpus et al. [10] extended the theoretical analysis of Burkov et al. by augmenting the model with parameters determined through photoemission spectroscopy. In the case of Karpus, they fit a standard Drude model to the flat conductivity at low frequency. Timusk et al. [15] reinterpret the linear optical conductivities in terms of massless 3D Dirac points. In this work, we too model the interband transitions as a series of Lorentz oscillators when fitting our high-frequency data; in addition, the generalised Drude model is modified to fit data across all frequencies.

2. Experiment

Samples of i-$GdCd_{7.98}$, $GdCd_6$ and YCd_6 were grown, using a high-temperature flux technique, and characterised at Ames Laboratory [11]. When cleaned and annealed, the quasicrystal showed a nearly flat temperature dependence in the resistivity [16]. The approximants also have a metallic temperature dependence with a low residual resistivity ratio very similar to Mori et al. [17]. The crystals were large with facets of a few millimetres. These samples were chosen because they could be grown to the sizes needed for optical spectroscopy.

To remove residual flux from the surfaces of the crystals, due to the growth process, the crystals were mechanically polished in stages of 9 μm, 3 μm, 1 μm, 250-nm and 30-nm grit using standard mechanical polishing techniques. Optical spectroscopy was performed using an IFSv/66 Bruker spectrometer from 20 cm^{-1} to 7500 cm^{-1} and, a Woolam M-2000 spectroscopic ellipsometer from 0.7 to 5 eV. Although measurements were performed at temperatures as low as 15 K in the 60 to 700 cm^{-1} region, there were not substantial differences from measurements performed at room temperature, so the low temperatures are not shown here.

The reflectivities for the QC and the approximants are displayed in Figure 1. The three curves have some common features. At the lowest frequencies, the reflectivities are near unity as is expected of materials with free electrons. The reflectivities drop over several hundred meV, suggesting a small number of free carriers, before levelling off between 0.6 and 0.7. Below 200 meV, the quasicrystal reflectivity drops below that of the approximants by several per cent. The quasicrystal reflectivity turns up around 3.5 eV. Both approximants show an increase in reflectance of $\approx$2% around 1.3 eV. Previous work on QCs has shown that high-frequency ellipsometry is affected by the type of surface treatment and with special treatment the reflectance drop (traditionally associated with the plasma frequency) was moved up to 7 eV [10]. We also see this surface sensitivity in our ellipsometry measurements, which did not give reasonable results above where our data ends in the figures and are thus omitted. This corresponds to a wavelength of

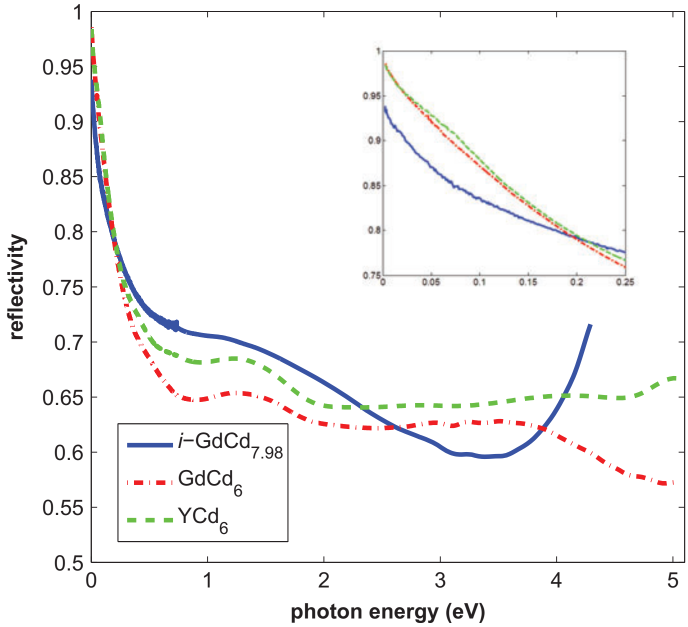

Figure 1. (colour online) Room temperature reflectivity of *i*-$GdCd_{7.98}$, $GdCd_6$ and YCd_6 determined from reflectance and ellipsometry measurements. Inset: low-frequency view of reflectivity to illustrate differing behaviour.

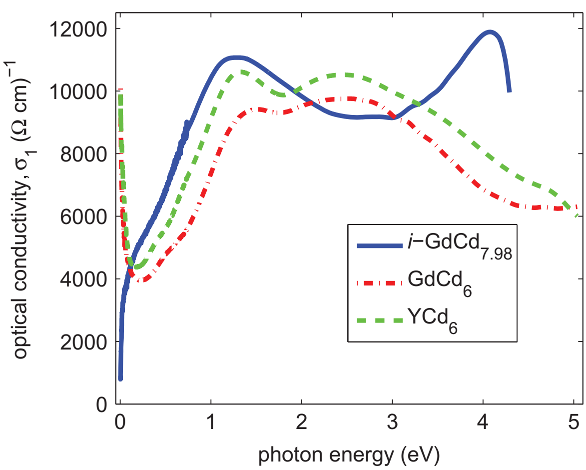

Figure 2. (colour online) Real part of the optical conductivity of *i*-$GdCd_{7.98}$, $GdCd_6$ and YCd_6 via Kramers-Kronig analysis of reflectivity in Figure 1. Note the contrast, at low frequency, between the metal-like approximant and the almost insulating quasicrystal.

approximately 250 nm, which is nearly identical to our second smallest polishing grit size, which suggests our 30-nm grit polish was ineffective.

The optical conductivities of the approximants, $GdCd_6$ and YCd_6 (Figures 2 and 3) both have a zero-frequency peak with an amplitude of 10,100 and 9900 $(\Omega\ \mathrm{cm})^{-1}$, respectively.

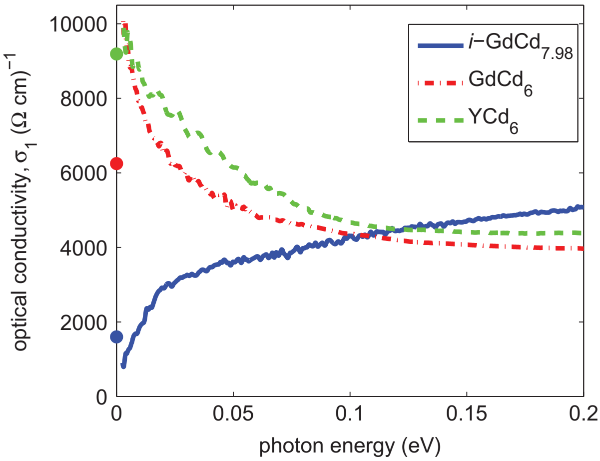

Figure 3. (colour online) Same data as Figure 2 below 200 meV, including DC values as filled circles, for the real part of the optical conductivity of *i*-$GdCd_{7.98}$, $GdCd_6$ and YCd_6. The DC values have an estimated uncertainty of 30% and are excluded from the analysis below.

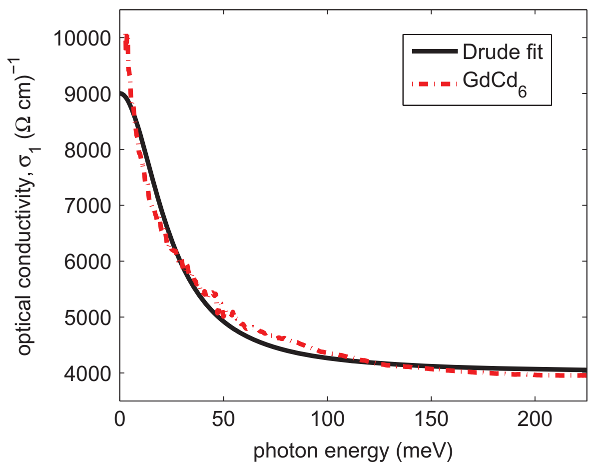

Figure 4. (colour online) An example of a Drude fit plus a constant term to the low frequency data of $GdCd_6$. The Drude model does not fit well and, in particular, does not have the proper curvature at low frequency.

Peaks such as these would typically be fit with a Drude model. There is a local minimum at 200 meV and two maxima between 1 and 3 eV. The *i*-$GdCd_{7.98}$ quasicrystal exhibits a minimum in the optical conductivity (Figures 2 and 3) of 800 $(\Omega\ \mathrm{cm})^{-1}$ at 3 meV, which is the low-frequency limit of our data. There are two maxima at 1.3 eV and 4.1 eV which exceed the amplitudes of the approximant peaks. Interestingly, this quasicrystal does not have a linear optical conductivity between 0 and 1 eV, unlike other quasicrystals lacking a low-frequency peak [15].

In all other cases, icosahedral quasicrystals and their approximants do not show such unequivocal zero-frequency peaks. Others have found either no Drude peak in icosahedral quasicrystals and their approximants, or have fit Drude peaks with very large scattering

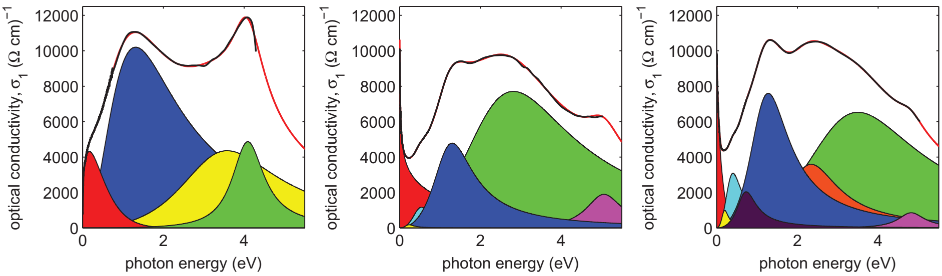

Figure 5. (colour online) Representative oscillator fits to the real part of the optical conductivity of *i*-$GdCd_{7.98}$(left), $GdCd_6$(centre) and YCd_6(right). The filled curves are the individual oscillators. The red area represents the GDM; all others represent Lorentz oscillators. The black line is the experimental data and the red line is the sum of the oscillators that are fit to the black line.

rates resulting in nearly flat optical conductivities. To be explicit, we found peaks in $GdCd_6$ and YCd_6 that have amplitudes of several thousand $(\Omega\ \mathrm{cm})^{-1}$, from the zero-frequency peak to the first local minima; whereas, others have, at best, an amplitude of a couple hundred $(\Omega\ \mathrm{cm})^{-1}$ from peak to minima, which is comparatively a flat response.

The room temperature DC conductivities are measured with a standard four-probe technique that has an estimated uncertainty of 30%. Our AC conductivities at our lowest frequency are within 50% of the DC values, which is acceptable given the uncertainty of the measurements. The approximant YCd_6 has a $\sigma_{DC} \approx 9200\ (\Omega\ \mathrm{cm})^{-1}$ and a $\sigma_{AC} \approx 9900\ (\Omega\ \mathrm{cm})^{-1}$; whereas, $GdCd_6$ has a $\sigma_{DC} \approx 6250\ (\Omega\ \mathrm{cm})^{-1}$ and a $\sigma_{AC} \approx 10,100\ (\Omega\ \mathrm{cm})^{-1}$. The quasicrystal *i*-$GdCd_{7.98}$ has a $\sigma_{DC} \approx 1600\ (\Omega\ \mathrm{cm})^{-1}$ and a $\sigma_{AC} \approx 800\ (\Omega\ \mathrm{cm})^{-1}$.

3. Analysis

The optical conductivities of both $GdCd_6$ and YCd_6 have a distinct peak at low frequency, which has only been unequivocally seen in decagonal approximants in the periodic direction [7]. Interestingly, unlike the decagonal approximant peaks, our peaks cannot be fit with traditional Drude theory (Figure 4). They can be fit to the generalised Drude model with a fractional power law, derived by Mayou, to account for the character of electron diffusion in quasicrystals and their approximants.

According to Mayou [18], at high frequencies, the electron diffusion must physically return to the well-known Drude form of $\alpha = 1$, since high frequencies correspond to short time scales. At small times, the wave packet has not spread far and thus the time evolution of the wave packet spreading is not suppressed yet. However, Mayou's GDM, as presented in Equation (2), is a low-frequency model since most values of α will give, via the optical sum rule, an infinite plasma frequency.

To fit our experimental data, we give the diffusion parameter a frequency dependence of $\alpha = \alpha_1 + \alpha_2\omega$ to return it to the standard Drude form at high frequencies; where α_1 is between -1 and 1, and α_2 is a small positive value that returns α to 1 beyond the low-frequency region.

The data were fit with Lorentz oscillators in the interband transition region to include the possible effects of low-frequency components of interband transition. Note that due to the freedom in fitting many oscillators, the fit is not unique therefore multiple different

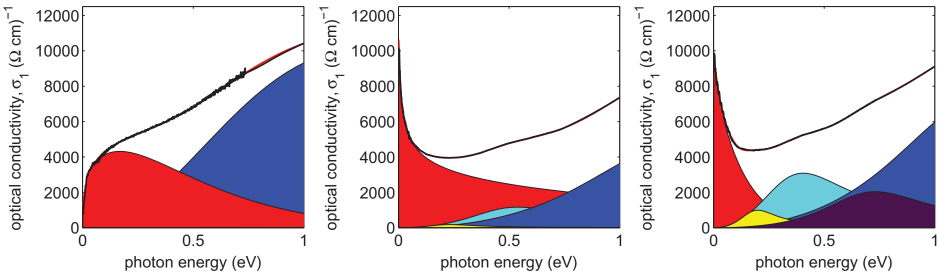

Figure 6. (colour online) Low-frequency regions of the representative oscillator fit to the real part of the optical conductivity of *i*-$GdCd_{7.98}$(left), $GdCd_6$(centre) and YCd_6(right). The filled curves are the individual oscillators. The red area represents the GDM; all others represent Lorentz oscillators. The black line is the experimental data and the red line is the sum of the oscillators that are fit to the black line.

Table 1. Estimate of bounds on the diffusion parameter α for *i*-$GdCd_{7.98}$, $GdCd_6$ and YCd_6. Using $L(t) \propto t^{\frac{\alpha+1}{2}}$, we can infer the time evolution of the electron from these bounds.

Sample	α_{lower}	α_{upper}
i-$GdCd_{7.98}$	−0.6	−0.2
$GdCd_6$	0.16	0.6
YCd_6	0.06	0.5

IBT oscillator combinations are used throughout the analysis. For the approximants and quasicrystals, no Lorentz oscillators are fit below 100 meV and 200 meV, respectively.

With the large amount of freedom of the many oscillators, we can only put a bound on the values of α_1 by requiring that the optical sum rule of the GDM be lower than some chosen plasma frequency, defined by

$$\frac{\omega_p^2}{8} = \int_0^\infty \sigma_{1,GDM}\, d\omega = \frac{\pi n e^2}{2m} \tag{3}$$

where ω_p is the plasma frequency, $\sigma_{1,GDM}$ is the optical conductivity of the GDM, n is the number density of the conduction electrons and m is the mass of the electron. Using Equation (3), the calculated plasma frequencies for *i*-$GdCd_{7.98}$, $GdCd_6$ and YCd_6 are 11.6, 11.5 and 11.6 eV, respectively. Being conservative and rounding these up to 15 eV, the acceptable α_2 values are those that give a plasma frequency below 15 eV given by the integral in Equation (3). In Figures 5 and 6, we show typical final fits, with the GDM and individual Lorentz oscillators shown. Repeating this analysis for numerous IBT fits, we estimate the bounds on the diffusion parameters α at zero frequency in Table 1.

We can see from Table 1 that in the large unit cell approximants, the electrons are travelling weakly to moderately superdiffusively, which is unlike the strong superdiffusion of the Drude model seen in small unit cell metals [18]. Further, the quasiperiodic lattice with its infinite unit cell size has the electron transport suppressed even more into the subdiffusive regime. Both approximants show similar bounds, which is expected, as the materials are quite similar: their lattice constants only differ by 0.055 Å [17]. If one were to conduct a photoemission analysis similar to Karpus analysis of interband transitions, it may be possible to reduce the size of these estimated bounds.

In summary, we have found a unique example where an almost insulating quasicrystal is paired with conducting approximants. Analysis of the conductivity shows a free carrier response that is best described by a non-Drude form. A generalised Drude model of Mayou that allows for quantum diffusion of the wave packets describes the data for both the quasicrystal and its approximants. Further characterisation of other quasicrystals and approximants from this family may allow trends to be determined and allow one to explore why these particular quasiperiodic and approximant lattices are dramatically different, whereas all other previous icosahedral families lacked these differences.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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