Anisotropic Optical Conductivity of Decagonal Quasicrystals

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The optical conductivity of high quality decagonal quasicrystals of $Al_{65}Co_{17}Cu_{18}$ and $Al_{62}Co_{15}Cu_{20}Si_3$ shows a strong anisotropy between the periodic and the quasiperiodic directions. We suggest that this is due to the dramatic enhancement of scattering in the quasiperiodic planes. The analysis of the conductivity reveals a drastic difference between the electronic structure of the decagonal quasicrystals and the icosahedral quasicrystals.

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The electronic properties of the icosahedral quasicrystals are different from those of metals and semiconductors as revealed by transport [1] and optical [2] studies. However, it is still unclear to what extent the unusual behavior of these materials can be attributed specifically to the quasiperiodicity. Decagonal quasicrystals combine two types of crystalline order: they are quasiperiodic in a plane and they are periodic in the direction perpendicular to the plane and as a result the differences in the physical properties associated with the periodic and the quasiperiodic translational symmetry may be studied in the same sample. The transport measurements of several different decagonal materials have established a marked anisotropy [3–7].

In this Letter we report for the first time on the optical conductivity of the decagonal phase of the selected Al-Co-Cu-(Si) alloys. The anisotropy of the conductivity may be attributed to the dramatic enhancement of scattering in the quasiperiodic planes. We also show that the optical properties of the decagonal quasicrystals exhibit a qualitative difference from those of the icosahedral materials [2,8–10]. The pseudogap near the Fermi level, which seems to be a characteristic of the icosahedral system, is not well developed in the decagonal Al-Co-Cu-(Si). As a result, free carriers contribute to the far infrared (FIR) conductivity both in the periodic and the quasiperiodic directions. This implies that the electronic properties of decagonal and icosahedral quasicrystals are very different.

High quality single grained samples of about $1.5\times1.5\times3$ mm^3 were separated from the slowly solidified ingots of nominal compositions $Al_{65}Co_{15}Cu_{20}$ and $Al_{62}Co_{15}Cu_{20}Si_3$. The measured composition of the decagonal grains were $Al_{65}Co_{17}Cu_{18}$ and $Al_{62}Co_{15}Cu_{20}Si_3$, respectively. In the following we designate the Si-free samples as ACC and Si-containing samples as ACCS. Further details concerning the solidification and the characterization of these alloys are reported elsewhere [11].

The reflectance measurements of the mechanically polished decagonal grains were carried out for the **E** vector both along the quasiperiodic planes and along the periodic direction in the frequency range between 30 and 40 000 cm^{-1}. Room temperature reflectivity spectra are shown in Fig. 1. The temperature-dependent reflectance was studied only for the ACC sample. The real part of the complex conductivity $\sigma(\omega)$ was obtained through Kramers-Kronig (KK) analysis. In both polarizations, the reflectivity rises at low frequencies. However, it is only weakly frequency dependent from the near infrared up to the near ultraviolet where the absolute value of the reflectance is close to 50%. Since the maximum measured frequency is below the position of the plasma minimum in the reflectivity spectra, certain assumptions had to be made about the high-frequency reflectance for the purposes of KK analysis. Studies of the icosahedral Al-Cu-Fe and Al-Pd-Mn quasicrystals revealed that the plasma

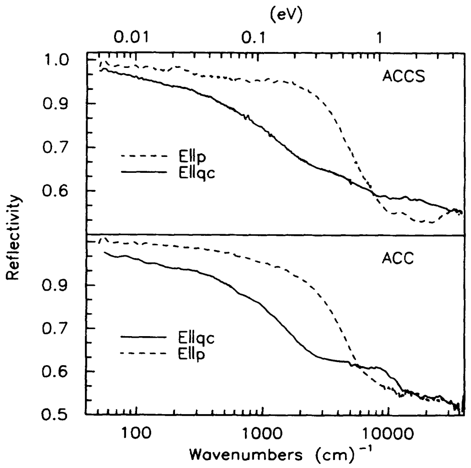

FIG. 1. The polarized light reflectivity spectra of the decagonal ACC and ACCS measured at room temperature.

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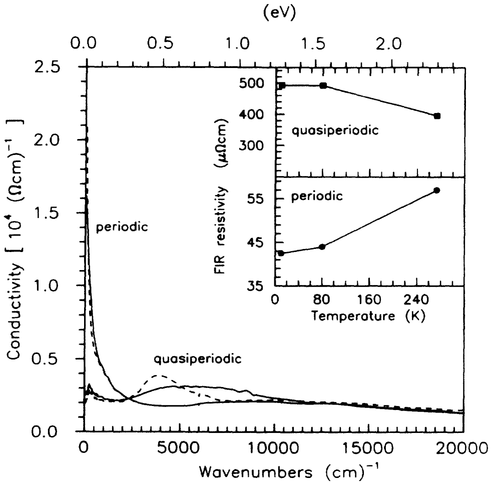

FIG. 2. The optical conductivity of the decagonal $Al_{65}Co_{17}Cu_{18}$ quasicrystal for the periodic and the quasiperiodic directions. Solid lines: $T = 300$ K; dashed lines: $T = 10$ K. Inset: the FIR resistivity for the periodic and quasiperiodic directions.

minimum is located around 70 000 cm^{-1} [10,12] which we use for the high-frequency extrapolation. At even higher frequencies the usual $1/\omega^4$ law of the reflectance dependence was used. We found that in the frequency range up to 20 000 cm^{-1}, the conductivity spectra are not significantly affected by assumptions about the exact shape of the plasma edge.

The frequency dependent conductivity of the two materials is shown in Figs. 2 and 3. The anisotropy of the conductivity is most prominent at low frequencies. At room temperature, as $\omega \rightarrow 0$, the ratio of the periodic and the quasiperiodic conductivities σ_p/σ_{qp} has been found to be as high as 4 for ACCS and 7 for ACC. At $T = 10$ K, the conductivity anisotropy of the ACC sample increases up to 12. At frequencies higher than 15 000 cm^{-1}, the anisotropy vanishes.

We estimated the ratio of n_e/m^* where n_e is the density of electrons and m^* is their effective mass from the model independent oscillator strength sum rule:

$$\int_0^\infty \sigma(\omega)\, d\omega = \frac{4\pi^2 n_e}{m^*}. \tag{1}$$

Integration of the periodic and of the quasiperiodic conductivities up to 20 000 cm^{-1} yields *equal* values of n_e/m^* ratio for each compound. This suggests that the effective mass is isotropic. Therefore, we conclude that band structure is not a dominant factor in determining the anisotropic optical conductivity of decagonal ACC and ACCS. The n_e/m^* values obtained in this way are as high as 3.1×10^{22} cm^{-3} for ACC and 3.3×10^{22} cm^{-3} for ACCS. These estimated values are smaller than those obtained using a similar procedure for the icosahedral Al-Mn-Si and Al-Pd-Mn [8,10].

The periodic conductivity at low frequencies is dominated by free carriers (Drude behavior) and may be written as follows:

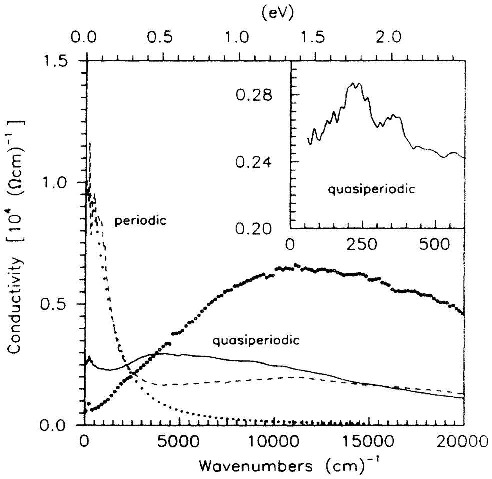

FIG. 3. The optical conductivity of the decagonal $Al_{62}Co_{15}Cu_{20}Si_3$ quasicrystal for the periodic (short-dashed line) and the quasiperiodic (solid line) directions. Filled dots: fit of the periodic conductivity with the Drude model as described in the text. Open dots: the conductivity of the icosahedral AlCuFe taken from Ref. [2]. Inset: the quasiperiodic conductivity in the FIR part of the spectrum.

$$\sigma(\omega) = \frac{\omega_p^2 \tau/4\pi}{1 + i\omega\tau}, \tag{2}$$

where ω_p is the free carrier plasma frequency and $\hbar/\tau$ is the scattering rate. The presence of the Drude feature in the periodic conductivity can be used to evaluate directly the free carrier scattering rate $\hbar/\tau_p$ which characterizes the influence of defects on transport and optical properties. Note that such estimates are not possible for icosahedral quasicrystals since the Drude absorption was not observed. Thus, the effect of defects on transport properties still remains unclear. (The conductivity of the icosahedral $Al_{63.5}Cu_{24.5}Fe_{12}$ from Ref. [2] is shown in Fig. 3). Equation (2) gives a good fit to the experimental data for $\sigma_p(\omega)$ of both decagonal quasicrystals in FIR. This yields the values of $\hbar/\tau_p$=400 cm^{-1} for ACC at $T = 300$ K and 1300 cm^{-1} for ACCS. At low temperatures, where the phonon contribution to scattering vanishes, the value of $\hbar/\tau_p$ in the ACC decagonal phase decreases to 230 cm^{-1}. This is only slightly larger than impurity scattering rate of high purity aluminum ($\hbar/\tau$=70 cm^{-1} at $T = 4$ K) [13]. The low values of $\hbar/\tau_p$ distinguish the decagonal system from the amorphous metals which can have scattering rates as high as several tens of thousands of wave numbers [14]. Therefore we suggest that the role of defects in the electronic properties of ACCS, and especially of ACC, is insignificant.

The values of the plasma frequency [$\omega_p = (4\pi n_{\rm fr} e^2/m^*)^{1/2}$] obtained from the Drude fit of the periodic conductivity are 19 000 cm^{-1} for ACC and 27 000 cm^{-1} for ACCS. Even by assuming that m^* is close to the free electron mass [15] we obtain the values of free carrier concentration n_{fr} to be equal to 9.4×10^{21} cm^{-3} for ACC and 1.3×10^{22} cm^{-3} for ACCS. These values are at least *2 orders of magnitude above* those reported for the high quality icosahedral quasicrystals [1]. The low values of free carrier concentration observed in the icosahedral materials were attributed to the opening of the pseudogap at the Fermi surface. The comparison of n_{fr} values reported for the icosahedral compounds with those observed in the periodic conductivity of ACC and ACCS suggests that the pseudogap is not well developed in the decagonal quasicrystals.

At frequencies above 1500 cm^{-1}, the periodic conductivity of both materials is dominated by the interband transitions and shows a smooth peak at 12 000 cm^{-1}. We will not discuss the interband absorption here.

The inset of Fig. 2 shows the FIR resistivities (ρ_p and ρ_{qp} for the periodic and quasiperiodic directions, respectively) derived from the optical conductivity at ω=50 cm^{-1}. The values of ρ_p in ACC agree with earlier results of direct dc measurements [4,5], but our ρ_{qp} value is slightly higher. The temperature dependence of ρ_p is typical for phonon scattering with a linear increase with temperature above 100 K and a saturation due to impurities at low temperature. The quasiperiodic resistivity is constant below 80 K and, in contrast with the periodic direction, *decreases* with temperature from 500 $\mu\Omega$ cm at 80 K to 400 $\mu\Omega$ cm at 300 K. This behavior has been explained in terms of the phonon assisted hopping [5].

The frequency dependence of the quasiperiodic conductivity is strikingly different from that in the periodic direction as well as from the conductivity of the icosahedral Al-Cu-Fe, Al-Mn-Si, and Al-Pd-Mn [2,8–10]. Neither a sharp Drude feature, as observed in the periodic conductivity, nor a steady rise of $\sigma(\omega)$, as found in the icosahedral quasicrystals, is manifested in the quasiperiodic conductivity of both ACC and ACCS where σ_{qp} is only a weak function of frequency. The behavior of the quasiperiodic conductivity is consistent with the optical data for disordered and amorphous metals, where the high value of the scattering rate makes $\sigma(\omega)$ flat and featureless [14]. Also, the absolute values of $\sigma_{qp}(\omega \rightarrow 0)$ are more typical of amorphous metals than of the high quality icosahedral quasicrystals, with the dc conductivity below Mott minimum-metallic conductivity [16].

The dc conductivity within the Drude model can be written as

$$\sigma(0) = n_e e^2 \tau / m^* . \tag{3}$$

We note that Eq. (3) is also a consequence of the semiclassical model of conduction in metals with an isotropic effective mass, and implies no assumptions about periodicity [17]. The sum rule analysis [Eq. (1)] of the conductivity of both materials suggests that the anisotropy of the conductivity due to band structure effects may be neglected. We are therefore able to attribute the anisotropy of the dc conductivity between the periodic and quasiperiodic directions, to the scattering rate which follows from Eq. (3). The magnitude of the scattering rate in the quasiperiodic planes $\hbar/\tau_{qp}$ should be about 4000 cm^{-1} both in ACC and ACCS to account for both the suppressed dc conductivity and nearly flat frequency dependence below 2000 cm^{-1}.

The anisotropy of the scattering rate is not consistent with typical defect scattering in disordered metals which is believed to be essentially isotropic. The enhancement of the quasiperiodic scattering rate over the impurity value found in the periodic conductivity by more than an order of magnitude suggests that quasiperiodic translational symmetry suppresses the lifetime of the free carriers. Unusual (anisotropic) scattering was discussed as a possible mechanism for the violation of the Wiedaman-Franz law as observed in the thermal conductivity measurements of the decagonal ACC and Al-Ni-Co [6]. We also point out that a value of $\hbar/\tau$ of the order of 4000 cm^{-1} may bring in weak localization effects in the quasiperiodic conductivity.

Both the stability of the icosahedral quasicrystals and their unusual electronic properties have been attributed to band structure effects. This leads to the opening of 0.5 eV pseudogap at the Fermi surface as the result of Fermi-surface–Jones-zone boundaries (FS-JZB) interaction [1,18–20]. In the icosahedral quasicrystals, both the Fermi surface and the Jones zone are nearly spherical. This is a favorable condition for the opening of a (pseudo)gap [1]. In the decagonal quasicrystals, the Jones zone is less symmetrical [21] suggesting that much of the Fermi surface is not distorted by the FS-JZB interaction.

The theoretical results on the pseudogap in the decagonal quasicrystals are controversial. Calculations based on the same structural model of the decagonal phase have revealed evidence for a pseudogap [22] while other studies have found no pseudogap [23]. Obviously more experimental survey is required to clarify the issue. A gapless Fermi surface is in accord with our observation of metallic concentration of free carriers. Moreover, the frequency dependence of both periodic and quasiperiodic conductivities is not consistent with the pseudogap and differs drastically from that of icosahedral compounds where such consistency has been found [8,24].

The experimental results presented above clearly offer a striking difference between the band structure of icosahedral quasicrystals and of decagonal ACC and ACCS. These results indicate that there is no well defined pseudogap in the decagonal materials. By contrast, the structurally ordered icosahedral quasicrystals show behavior accordant with a semiconducting gap behavior [25].

An important insight into the dynamic conductivity in the quasiperiodic planes is provided by the phonon structure observed in the infrared region. This structure is shown in the expanded scale in the inset of Fig. 3 for the ACCS sample. The infrared-active phonons give rise to sharp peaks in $\sigma(\omega)$ in the crystalline materials, including the approximant phase of Al-Si-Mn [8], and the simple crystal of Al_2Ru [25]. In contrast, a broad structure is found in $\sigma_{qp}(\omega)$. The frequency position of the structure, as well as of the similar feature observed in the icosahedral quasicrystals [2], is close to the location of the maximum in the phonon density of states of Al. Similar effects are observed in amorphous semiconductors [26], where phonon contribution to the conductivity appears to be proportional to the phonon density of states. In an amorphous material, momentum selection rules are violated and all phonons contribute to the optical conductivity. The lifetime of the IR active modes is in effect suppressed. The observation of the broad feature associated with the phonon density of states in the decagonal conductivity of ACC and ACCS suggests that the effect of quasiperiodicity on phonons and as well as free carriers is equivalent to very strong disorder or amorphization. Our results are closely related to recent observations of the anomalous behavior of high frequency phonons in inelastic neutron experiments and Mössbauer spectroscopy [27,28].

Since the in-plane momentum is not conserved in the decagonal quasicrystals, whereas the periodic momentum is still a good quantum number, the distribution of states within the Fermi sphere can be considered as a set of quasi-two-dimensional planes separated along the z direction by $2\pi/L$, where L is the system size. Such an arrangement of states would give rise to the infinite z conductivity (in the absence of scattering) while the in-plane conductivity would approach a weak-localization regime. This is in an agreement with the experimental results plotted in Fig. 2 and Fig. 3 as discussed above. Moreover, this model of the electronic states is in qualitative agreement with weak localization behavior found in the magnetoresistance [7].

In conclusion, the analysis of the optical conductivity shows no evidence for a well developed pseudogap near the Fermi level in the Al-Co-Cu-(Si) decagonal quasicrystals. The anisotropy of the conductivity of these materials may arise from the dramatically enhanced scattering due to the quasiperiodic order. Phonons and free carriers seem to be affected by the quasiperiodicity in a similar way; in both cases the lifetimes are strongly suppressed. Though this is likely to be true also for the icosahedral compounds, there is a considerable difference in the properties of these two families of quasicrystals. This originates mainly from the density of states reduction due to the pseudogap in the icosahedral materials. An unresolved question related to the understanding of localization in quasicrystals may be stated as follows: Provided that two-dimensional quasicrystals have metallic properties along the periodic z axis, can the conductivity in the quasiperiodic planes be below the minimum metallic conductivity σ_M?

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