Optical Conductivity of Insulating Al-Based Alloys: Comparison of Quasiperiodic and Periodic Systems

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We report on the optical conductivity of the structurally ordered icosahedral quasicrystal $Al_{70}Pd_{20}Re_{10}$ and the crystal Al_2Ru obtained from the reflectance measured over a wide frequency range. Our results show that both the crystal and the quasicrystal are semiconductors and have quite similar band structure. The major difference between the two materials arises from the localization of the electronic states deep inside the band gap of the quasicrystal in spite of the metallic carrier density. We speculate that the quasiperiodic symmetry favors carrier localization.

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A variety of Al-based quasicrystals and their crystalline approximants show unusual electronic properties which seem to be different from those of metals and semiconductors [1,2]. Attempts to observe specific electronic effects in quasicrystals (QC) through the comparison with approximant phases have not been successful [1,3,4]. In particular, the dc conductivities of stable QC phases are very close to those of approximants [1,4]. Also, the optical properties of the metastable Al-Mn-Si phases have been found to be similar for the icosahedral QC and its approximant [3]. Though the approximants can be quite close compositionally to the icosahedral phases, they are still complicated structurally and have a primitive cell consisting of more than a hundred atoms. This complexity as well as any residual sample imperfections, especially important for the metastable systems, may account for the basic similarity between approximants and QC. Nevertheless, recent studies of the stable, *structurally ordered* icosahedral $Al_{70}Pd_{20}Re_{10}$ [5] and the orthorhombic crystal of Al_2Ru [6] with only 6 atoms per primitive cell indicated certain differences in the transport properties between the quasicrystal and the crystal. The content of Al and heavy transition metals in the two materials is comparable. The structural order of both materials has been characterized by x-ray measurements and by low-temperature dc conductivity σ_{dc} which is about *two orders of magnitude* below the lowest values reported for the stable icosahedral compounds [7]. In view of the diminished role of defects in the structurally ordered materials, and since the behavior of Al_2Ru cannot be attributed to crystallographic complexity, a comparative study of $Al_{70}Pd_{20}Re_{10}$ and Al_2Ru may provide an insight into the influence of the quasiperiodicity on the electronic properties.

In this Letter we present evidence, based on optical measurements, that both $Al_{70}Pd_{20}Re_{10}$ and Al_2Ru are semiconductors with a direct gap close to 1 eV while the minimum indirect band gap is about 0.2 eV. Whereas the band structure of both compounds is quite similar, there appears a remarkable difference in the low-frequency (and consequently, the low-temperature) properties which, we suggest, arises from the localization of electronic states inside the band gap of the quasicrystal.

The details of preparation and characterization of the structurally ordered $Al_{70}Pd_{20}Re_{10}$ [5] and Al_2Ru [6] have been reported elsewhere. Reflectivity spectra of both materials have been measured over the frequency range 16–48 000 cm^{-1}, and are shown in Fig. 1. The reflectivity of crystalline Al_2Ru resembles that of a semiconductor with sharp phonon peaks in the far infrared (FIR) and gaplike feature around 10 000 cm^{-1}. The spectrum of icosahedral $Al_{70}Pd_{20}Re_{10}$ exhibits weaker phonon structure.

The results of the Kramers-Kronig (KK) analysis for the real part of the complex conductivity $\sigma(\omega)$ are shown in Fig. 2. For the high-frequency extrapolation we used the reflectance of the icosahedral Al-Pd-Mn [8]. We found that the conductivity for $\omega < 20\,000$ cm^{-1} is not

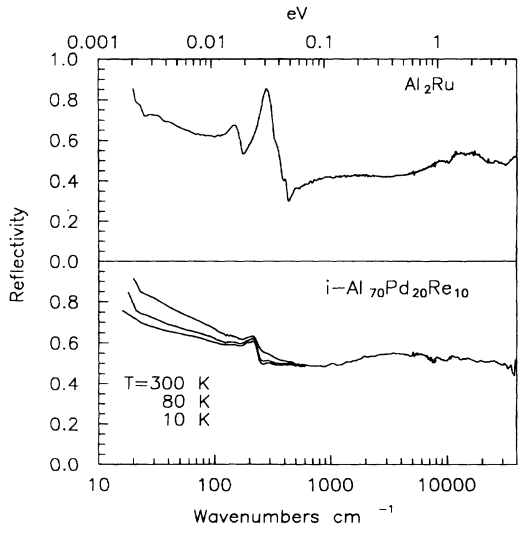

FIG. 1. The reflectivity of crystalline Al_2Ru at 300 K (upper panel) and of the icosahedral $Al_{70}Pd_{20}Re_{10}$ at various temperatures (bottom panel).

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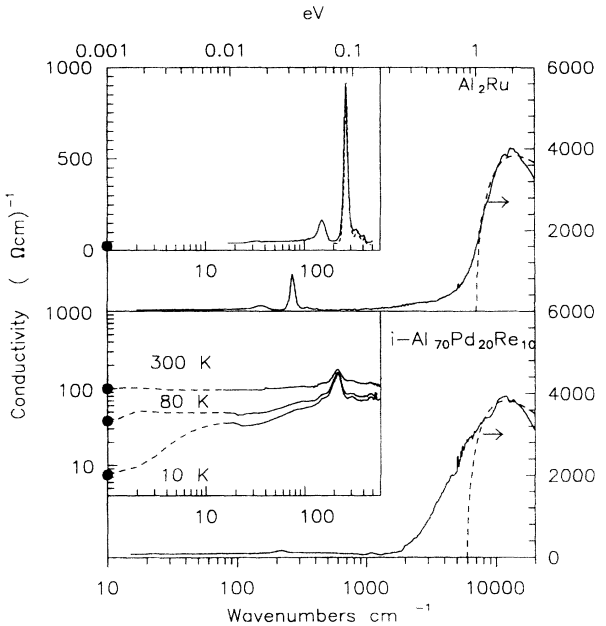

FIG. 2. Main panels: The optical conductivity of Al_2Ru (top panel) and of the icosahedral $Al_{70}Pd_{20}Re_{10}$ (bottom panel) at room temperature. Dashed lines show the calculated conductivity with the onset due to the direct gap. The inset of the top panel: FIR conductivity of Al_2Ru at room temperature (solid line) and at 10 K (dashed line). The inset of the bottom panel: FIR conductivity of $Al_{70}Pd_{20}Re_{10}$. Dashed lines show the region of the KK interpolation as explained in the text. The dots in the insets show the values of the dc conductivity.

affected by the assumptions regarding the exact shape of the high-frequency extrapolation. At low frequencies the reflectivity was extrapolated to $\omega = 0$ using the Hagen-Rubens formula.

The frequency dependence of the conductivity of both structurally ordered materials shows a low conductivity in the far infrared and midinfrared (MIR), and then exhibits a large peak, centered around 12 000 cm^{-1}. We also observe a clear onset at 2000 cm^{-1} (0.24 eV) in $\sigma(\omega)$ for $Al_{70}Pd_{20}Re_{10}$. Earlier studies of the icosahedral Al-Cu-Fe found an unusual *linear* frequency dependence of $\sigma(\omega)$ suggesting a behavior unique to QC [2]. However, subsequent work has shown that the linear conductivity can also be seen in the quasicrystal Al-Mn-Si as well as in its crystalline 1/1 approximant [3]. Furthermore, in a single grained sample of the quasicrystal Al-Pd-Mn the conductivity shows a power-law variation with a power that is greater than 1 [9]. A comparison of the available optical data for different QC indicates that the samples with lower σ_{dc} have smaller MIR conductivity and demonstrate stronger divergence from the linear law for $\sigma(\omega)$ [2,3,8,9]. This tendency is clearly supported by the data in Fig. 2. The main feature of the $\sigma(\omega)$ of both $Al_{70}Pd_{20}Re_{10}$ and Al_2Ru, the peak at 12 000 cm^{-1}, is narrower and more asymmetric than that of the earlier studied compounds. The asymmetry of this peak may be in accord with the excitations across the band gap E_g when $\sigma(\omega) = \text{const} \times (\sqrt{\omega - E_g})/\omega$ [10]. The dashed lines in the main panels of Fig. 2 illustrate the principal agreement of the square root behavior with the experimental data both for the crystal and QC. The gap values used in the calculation are $E_g = 6000\ cm^{-1}$ (0.74 eV) for $Al_{70}Pd_{20}Re_{10}$ and $E_g = 7100\ cm^{-1}$ (0.88 eV) for Al_2Ru. The consistency of the high-frequency properties of the materials suggests that the band structures of the crystalline and quasicrystalline systems are similar.

The deviation from the square root trend at low frequencies is more obvious for the QC. We suggest this, as well as the sharp onset at 2000 cm^{-1}, is due to transitions across an *indirect gap* of magnitude 2000 cm^{-1} (0.24 eV). An indirect gap of similar value in crystalline Al_2Ru is predicted by linear muffin tin orbital calculations [11] and observed in dc conductivity (Fig. 3) [5]. However, no corresponding feature in $\sigma(\omega)$ of Al_2Ru has been found or is expected because the selection rules based on the momentum k conservation make the probability of indirect transitions quite small [12]. If the selection rules are relaxed, indirect transitions will give rise to a $\sigma(\omega)$ of considerable absolute value [13]. Such relaxation occurs in amorphous systems and may also result from the localization of carriers participating in the transition. We suggest below that (i) the electronic states of $Al_{70}Pd_{20}Re_{10}$ taking part in 0.24 eV transition are localized, and (ii) the phonon structure of this material has a strong resemblance to that of amorphous semiconductors, in agreement with the view that k is not a good quantum number in the QC. Therefore, it seems quite plausible that the feature at 2000 cm^{-1} (0.24 eV) in $\sigma(\omega)$ of the QC may result from an indirect transition.

The FIR conductivity of $Al_{70}Pd_{20}Re_{10}$ is strongly temperature dependent as shown in the inset of Fig. 2. At room temperature $\sigma(\omega)$ is nearly constant below 200 cm^{-1} and matches the dc value well. As the temperature decreases, a mismatch between the FIR conductivity at the

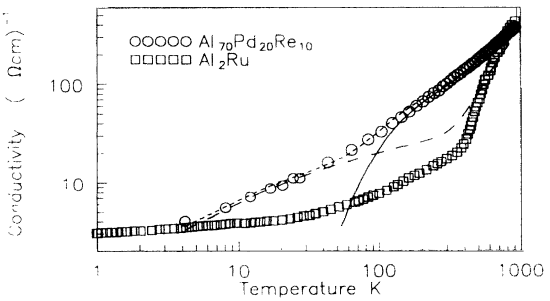

FIG. 3. The temperature dependence of the dc conductivity of Al_2Ru (squares) and of icosahedral $Al_{70}Pd_{20}Re_{10}$ (circles) from Ref. 5. The solid line is a fit with a simple gap model [Eq. (1)]. The activation energies used in the fit were obtained from the $\sigma(\omega)$ as described in the text. The short dashed line: The same fit but with the addition of the variable range hopping term. The long dashed line has been calculated assuming only contributions from the variable range hopping and the interband term with the energy E_1.

lowest measured frequency (16 cm^{-1}) and the dc value develops. The dashed lines in the inset of Fig. 2 show the KK interpolation—the result for $\sigma(\omega)$ in the frequency range where the reflectivity was extrapolated to the dc value. At $T = 10$ K the $\sigma(\omega)$ is no longer independent from frequency as the spectrum at $T = 300$ K but demonstrates a clear suppression of the absolute value in the far infrared frequencies. A region of strongly suppressed but nonzero conductivity that can be classified as a pseudogap is found in $\sigma(\omega)$ below 200 cm^{-1}. Since the concentration of carriers in $Al_{70}Pd_{20}Re_{10}$ is as high as 10^{20} cm^{-3} [5], one may expect to observe a Drude-like frequency dependence of the conductivity (Lorentzian-shaped oscillator centered at zero frequency) if these carriers act like free charge carriers. Instead, the conductivity shows evidence of a pseudogap. We emphasize that the pseudogap develops in the energy range well above the extrapolated region and is not connected with the particular form of the extrapolation. The appearance of a pseudogap may be associated with the energy E_2 separating localized states at the Fermi level and delocalized states at the mobility edge. According to Mott's arguments, this separation results in an activated behavior of σ_{dc} with the activation energy E_2 [14]. The frequency dependence of the low-temperature conductivity suggests that this energy E_2 is about 200 cm^{-1} in $Al_{70}Pd_{20}Re_{10}$.

Based on the $\sigma(\omega)$ data we expect to observe two activation energies in the temperature dependence of σ_{dc} of $Al_{70}Pd_{20}Re_{10}$: One due to the indirect gap $E_1 = 2000$ cm^{-1} (0.24 eV) and the other due to the mobility gap with $E_2 = 200$ cm^{-1}. This implies that the density of states (DOS) inside the band gap is finite which is consistent with the values $g_0 = 8 \times 10^{21}$ states eV^{-1} cm^{-3} as obtained from the specific heat measurements [5]. The preexponential factor of the E_2 process has to be equal to Mott's minimum metallic conductivity σ_M. We fitted the experimental dc conductivity shown in Fig. 3 as

$$\sigma_{dc} = A\exp(-E_1/kT) + B\exp(-E_2/kT), \qquad (1)$$

where A and B are constants. The best fit in the temperature range 90–950 K is obtained when $E_1 = 2100$ cm^{-1} (0.26 eV) and $E_2 = 250$ cm^{-1} which is in good agreement with $\sigma(\omega)$, showing the consistency between transport and optical data. The prefactor B was found to be 190 $(\Omega\ cm)^{-1}$ which is of the order of σ_M, therefore justifying the interpretation of the pseudogap as being due to the mobility edge; the prefactor A is equal to 1100 $(\Omega\ cm)^{-1}$. In contrast, the FIR conductivity of Al_2Ru is only weakly temperature dependent and shows no trace of a low-lying pseudogap. This is in accord with the temperature dependence of σ_{dc} which can be well described as a single activation process with an activated energy of 0.15–0.17 eV [5]. Thus the qualitative difference between the temperature dependences of σ_{dc} in the crystal and in the QC arise from the additional activation process due to a mobility gap as revealed by the frequency dependence of $\sigma(\omega)$ of the QC. The localization of the electronic states in the QC also explains the similarity of the values of σ_{dc} found in the QC and in Al_2Ru even with a carrier density in latter system [18] that is at least three orders of magnitude smaller than in $Al_{70}Pd_{20}Re_{10}$.

Figure 3 shows that Eq. (1) agrees with the experiments only at $T > 80$–90 K. Several possible scenarios can account for nonzero conductivity down to 1 K and for the observed temperature dependence. Confined electronic states in the QC may have a different degree of localization as opposed to the sharp threshold between localized and extended states within the Mott's picture. This is also in accord with relatively smooth features in $\sigma(\omega)$ dependence at 10 K which we assign as being due to the mobility gap. Another factor is the Coulomb interaction. With the high concentration of carriers and evidence that these carriers are localized, a Coulomb gap may become important. The estimated value of the Coulomb gap $\Delta = e^3 g_0^{1/2}/\kappa^{3/2}$ [15], given a dielectric constant $\kappa = 64$, from KK analysis of the reflectance, is then as high as $\Delta = 100$ K, which is at least an order of magnitude above that of amorphous semiconductors [15]. The experimentally observed finite density of states at the Fermi level at $T = 4.2$ K may be due to the much higher carrier concentration in the icosahedral systems than in amorphous semiconductors, which tends to enhance the absolute value of the DOS inside the Coulomb gap [16]. The above estimate shows that the energy range where the DOS may be distorted due to electron-electron interactions is quite significant. Finally, the variable-range hopping conductivity (VRH) may account for $\sigma_{dc}(T)$ at low temperature. The possible impact of the VRH is illustrated by the short dashed line in the inset of Fig. 3, obtained by adding an $\exp(-T_0/T)^{1/4}$ term to Eq. (1) with $T_0 = 1000$ K. It should be emphasized that VRH is the only important term for $T < 30$ K. This is illustrated by the long dashed line in Fig. 3 where the term associated with the mobility gap E_2 has been excluded, and the calculated dependence assumes contributions only from VRH and from the interband activation. It is quite clear that this dependence does not agree with the data in the temperature range from 30 up to 800 K, and an additional activation term is needed.

The above fits of the dc conductivity, as well as the onset in $\sigma(\omega)$ of $Al_{70}Pd_{20}Re_{10}$ at ≈ 2000 cm^{-1}, show that the minimal band gap in this QC, as well as in Al_2Ru, is of the order of 0.2 eV. Since $\sigma(\omega)$ in $Al_{70}Pd_{20}Re_{10}$ rises relatively slowly above 2000 cm^{-1} and diverges strongly from the square-root behavior, it seems unlikely that this is a direct gap in k space, whereas the analogy with Al_2Ru supports the suggestion of an indirect transition. These electronic properties of the QC are not predicted by band-structure calculations [17].

The phonon behavior in Al_2Ru and in $Al_{70}Pd_{20}Re_{10}$ also offers a striking contrast. We resolve four peaks, all with a half-width below 30 cm^{-1}, in the reflectivity and conductivity of Al_2Ru, whereas only one broader

feature with a reduced oscillator strength is found in the spectrum of the QC (Figs. 1 and 2). A suppression of the phonon oscillator strength in the amorphous glasses of As_2Se_3, as compared to the crystalline material of the same composition, has been reported [19]. This anomalous effect suggests that the mechanisms describing the process of interaction of light with phonons in a crystal may not apply for the QC's or amorphous compounds and that further study is required. The phonon-like feature in the spectra of $Al_{70}Pd_{20}Re_{10}$ is located close to the position of the maximum in the phonon density of states of pure Al. The smearing of the phonon peaks into a structure which resembles the phonon density of states is also typical for amorphous semiconductors [20] and is the result of the lack of momentum conservation which allows the interaction of light, not only with IR-active modes as occurs in crystals, but with all phonons. Such broad phonon structure located close to 200 cm^{-1} has been observed in other icosahedral and decagonal QC [2,3,8,9,21]. By contrast, sharp phonon peaks were found in the conductivity of the approximant phases [3]. If momentum is not a good quantum number in a quasilattice, or an amorphous material, the similarities in phonon behavior found in QC's and amorphous semiconductors is not surprising. This possibility with respect to QC has been discussed on theoretical grounds [22].

The improvement of the structural quality of icosahedral $Al_{70}Pd_{20}Re_{10}$ and crystalline Al_2Ru have made it possible to observe new electronic properties of the Al-based alloys using transport and optical probes. These measurements have allowed us to draw conclusions about the role of the quasiperiodicity in the electronic processes. The major difference in the properties of the crystal and of the QC occurs only at relatively low frequencies and can be summarized as follows: (i) the electronic states of the QC are localized and show a mobility gap; (ii) the phonon structure of the QC shows abnormal behavior suggesting relaxation of the momentum, whereas lattice modes of Al_2Ru demonstrate no anomalies; (iii) in the QC the indirect band gap gives rise to an $\sigma(\omega)$ of unusually high absolute value suggesting once again relaxation of k conservation; these points imply that momentum is not a good quantum number in the quasicrystal. We suggest the relaxation of momentum conservation is an intrinsic property of the quasilattice. We also speculate that quasiperiodic order is favorable for localization of charge carriers even in the regime of metallic carrier density. Additional evidence for this comes from an analysis of the optical conductivity of the decagonal QC which indicates that the quasiperiodic order is responsible for the dramatic decrease (by an order of magnitude) of the charge carrier lifetime as compared to the lifetime due to the impurity scattering in the same sample [21]. The impact of crystalline order or specific translational symmetry becomes less important at higher energies ($\omega > 0.1$ eV) where the conductivity of both the crystal and the QC is determined by band structure. This general tendency has also been revealed by studies of amorphous semiconductors which show clear evidence of a band gap characteristic of crystalline materials [14]. Thus, one finds a definite analogy between the electronic properties of amorphous semiconductors and insulating QC despite the large difference in their carrier density. The major contrast between QC and amorphous systems is that localization of the electronic states in QC is most obvious in *highly ordered* though nonperiodic materials and disappears when these materials are in an amorphous state [1]. The detailed behavior of the conductivity of a quasicrystal near the band gap and in the phonon region requires further investigation.

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