

## Optical Conductivity of the Stable Icosahedral Quasicrystal $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$

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The optical properties of the stable icosahedral quasicrystal  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  have been measured from 40 to  $25000\text{ cm}^{-1}$  at 300 K and at 80 K. Unlike metallic glasses with a Drude spectrum with strong elastic scattering by disorder, or semiconductors with a conductivity gap, the optical conductivity of this quasicrystal is distinctive: Starting from the very low dc value it increases linearly with frequency well into the near infrared. A prominent peak in the conductivity is observed at  $245\text{ cm}^{-1}$ ; its position and strength suggest that it arises from a direct excitation of phonons.

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The discovery of an icosahedral (*i*) phase in Al-Mn alloys [1], subsequently observed in many other metallic alloys [2], with a crystallographically forbidden symmetry has prompted the search for unusual electronic properties in this new class of materials. The combination of non-crystallographic symmetry (icosahedral, etc.) and sharp diffraction spots is the signature of a quasicrystal. The anomalous diffraction pattern observed in quasicrystals suggests that the electrons are strongly scattered and perhaps localized.

The Al-Cu-Fe alloys [3] are of special interest as they can be prepared as single-phase quasicrystals, the various physical properties of which have been reported [4]. Recently, Biggs, Li, and Poon reported on the dc transport of the new stable icosahedral alloy,  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  [5]. The resistivity of this material is  $2800\text{ }\mu\Omega\text{ cm}$  at room temperature and it increases linearly to  $4400\text{ }\mu\Omega\text{ cm}$  at 4.2 K, placing it near or below the "minimum metallic conductivity" estimated for these alloys [5,6]. Klein *et al.* [7] have found resistivities of the order of  $11000\text{ }\mu\Omega\text{ cm}$  at 4.2 K in this system and suggest that insulating and semiconducting quasicrystals could exist.

In this Letter we present the first results on the optical conductivity over a wide range of frequencies for the quasicrystal  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$ . The importance of the frequency-dependent conductivity in disordered systems has been emphasized by Mott and Davis [8]. The conductivity of the free carriers, in the presence of strong scattering, is predicted to deviate from the Drude form by a transfer of spectral weight from low frequencies to higher frequency, resulting in the formation of a pseudogap in the conductivity spectrum [9]. Mott cites the case of liquid tellurium [10] as evidence for this phenomenon. We will show that the quasicrystal  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  exhibits this effect in a more dramatic way.

Thin ( $\approx 20\text{ }\mu\text{m}$ ) ribbon samples  $\approx 2\text{ mm}$  wide were prepared by melt spinning in an inert atmosphere. The rapidly quenched material was then annealed to obtain single *i*-phase material. The phase purity was confirmed by x-ray diffraction. The ribbons produced in this manner had a rough surface and were very brittle. The

dc resistivity was  $4700\text{ }\mu\Omega\text{ cm}$  at 4.2 K decreasing to  $2800\text{ }\mu\Omega\text{ cm}$  at room temperature.

The reflectance of the samples was measured using an *in situ* gold and aluminum evaporation technique which corrects for most diffraction and geometry effects which arise due to the irregular surface of the sample [11]. Figure 1 shows the reflectance from 40 to  $25000\text{ cm}^{-1}$  at room temperature. The reflectivity decreases quickly with frequency to  $\approx 70\%$  by  $500\text{ cm}^{-1}$  and is then essentially constant up to  $25000\text{ cm}^{-1}$ . Note that with the exception of the shoulder at  $245\text{ cm}^{-1}$  the spectrum is featureless. The small fluctuations in the curves are due to noise and other instrumental artifacts. We also took data at 80 K and found that the reflectance at low frequency was  $\approx 5\%$  lower in magnitude and the shoulder

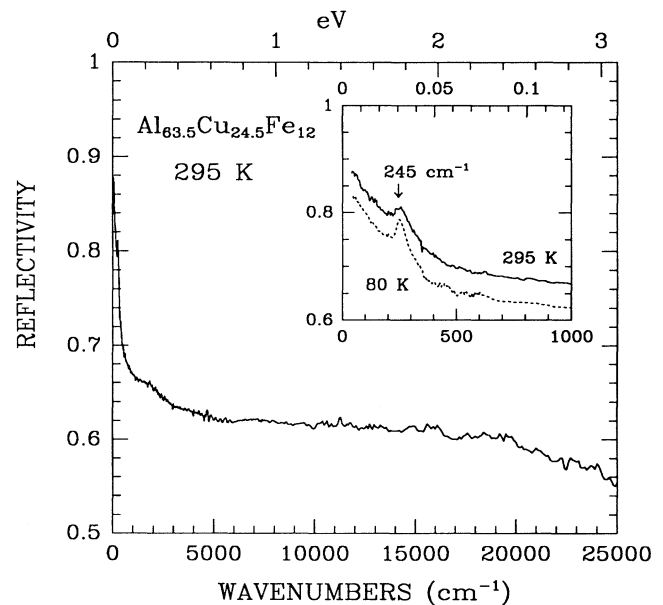


FIG. 1. The reflectivity of  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  at 295 K from 40 to  $25000\text{ cm}^{-1}$ . Inset: The reflectance at 295 K (solid line) and at 80 K (dashed line) on an expanded scale. The shoulder at  $\approx 250\text{ cm}^{-1}$  is clearly visible.

had sharpened and shifted down in frequency to  $240 \text{ cm}^{-1}$ . The room-temperature data at high frequencies are similar to previous work on Al-Mn quasicrystals by Frigerio and Rivory [12].

The optical conductivity was obtained by Kramers-Kronig analysis. To calculate the phase of the reflectance it is necessary to include data at all frequencies. We assumed that below our lowest measured frequency,  $40 \text{ cm}^{-1}$ , a limit set by the onset of diffraction effects due to our small sample, the material followed the Hagen-Rubens relation for a Drude model with a constant relaxation rate. We fitted the parameters to this extension to our measured optical data. Above the largest measured frequency,  $25000 \text{ cm}^{-1}$ , the data were extended using a Drude model with a plasma frequency near that of aluminum ( $\omega_p = 110000 \text{ cm}^{-1}$ ) with a large damping ( $\approx 40000 \text{ cm}^{-1}$ ), which was chosen to match the last measured data point. Different extrapolations involving copper and aluminum, with higher and lower reflectances than the Drude extrapolation, respectively (both scaled to match the last data point), were also examined. Below  $1 \text{ eV}$  the conductivity is insensitive to the nature of the high-frequency extrapolation, but at  $3 \text{ eV}$  the error in the conductivity is  $\approx 500 \Omega^{-1} \text{ cm}^{-1}$ .

The conductivity is shown in Fig. 2. The magnitude of the overall conductivity in the visible range of  $2$  to  $4.0 \text{ eV}$  is typical of most metals, i.e., of the order of  $10000$

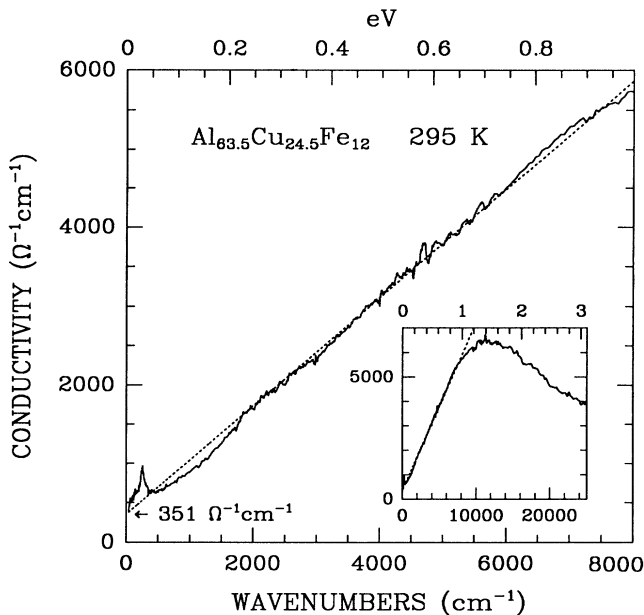


FIG. 2. The optical conductivity of the quasicrystal  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  at  $295 \text{ K}$  from  $40$  to  $8000 \text{ cm}^{-1}$  obtained by Kramers-Kronig analysis of the reflectance. The conductivity rises linearly from the low dc value to a magnitude of  $6000 \Omega^{-1} \text{ cm}^{-1}$ , a value typical for many metals in the visible. The dashed line is a least-squares fit to the data from  $40$  to  $7500 \text{ cm}^{-1}$ . Inset: The behavior of the conductivity over a larger frequency range.

$\Omega^{-1} \text{ cm}^{-1}$ . What is unusual is the total absence of a Drude free-carrier response at low frequency. Instead, the conductivity falls linearly over a frequency range of nearly three decades, from the visible to the far infrared, to meet the very low dc value, shown in the inset. The straight line is a least-squares fit to the data between  $50$  and  $7500 \text{ cm}^{-1}$ . The fit to the room-temperature data has a slope of  $0.69 \Omega^{-1}$  and a zero-frequency intercept of  $351 \Omega^{-1} \text{ cm}^{-1}$  which agrees well with the dc conductivity of  $357 \Omega^{-1} \text{ cm}^{-1}$ .

Figure 3 shows the low-frequency behavior of the optical conductivity at room temperature and at  $80 \text{ K}$ . Also shown in the figure is the least-squares-fitted straight line from Fig. 2 for the room-temperature data. A well-defined peak centered at  $245 \text{ cm}^{-1}$  dominates the conductivity. We suggest that this peak arises from a direct coupling of electromagnetic waves to phonons. The feature sharpens at low temperature and it is softened from  $245$  to  $240 \text{ cm}^{-1}$ . The decrease in frequency may be a result of strong electron-lattice interactions, which may have a role in the stability of these systems [13].

The frequency of  $245 \text{ cm}^{-1}$  is close to the  $271\text{-cm}^{-1}$  peak in the Al phonon density of states [14]. A concentration-weighted geometrical mean of the masses in the

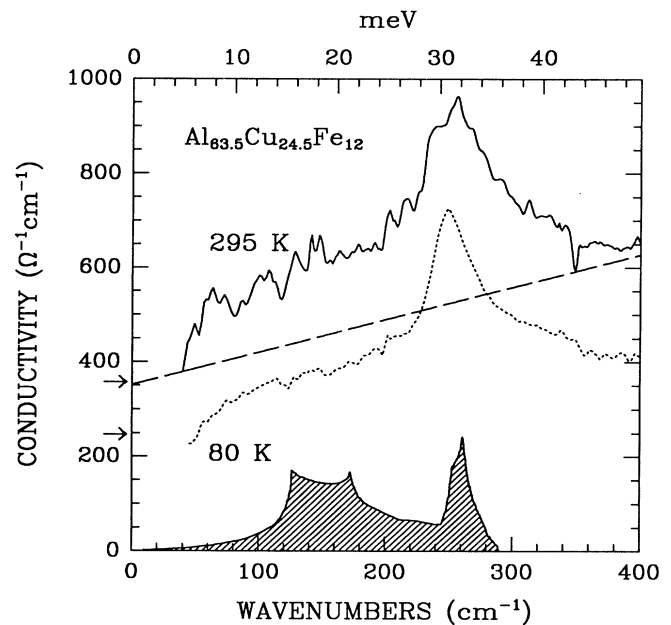


FIG. 3. The low-frequency optical conductivity of  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  at  $295 \text{ K}$  (solid line) and at  $80 \text{ K}$  (dotted line). The straight dashed line is the result of the least-squares fit to the room-temperature data shown in Fig. 2. The arrows indicate the measured dc conductivity at  $295 \text{ K}$  (top) and  $80 \text{ K}$  (bottom). The shaded area at the bottom of the figure is the phonon density of states in Al (with the frequency and amplitude adjusted for the different reduced mass in the formula). We believe the structure at  $250 \text{ cm}^{-1}$  and below is due to phonons activated by the quasicrystalline order.

$\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  reduces this frequency to  $260\text{ cm}^{-1}$  and is indicated by the shaded area in Fig. 3. The strength of the phonon structure is not far from what one expects from an optic phonon in a metal [15].

Another possibility is that the  $245\text{-cm}^{-1}$  structure may result from interband transitions between peaks in a spiky density of states predicted by Fujiwara [13]. Such peaks should exhibit a temperature dependence where the strength of the peak is controlled by the Fermi function. Going from room temperature to 80 K the intensity of the  $245\text{-cm}^{-1}$  peak drops by about 30% which is expected  $n(\omega)+1$  Bose factor for a phonon at  $245\text{ cm}^{-1}$ . A transition between two discrete electronic states that straddle the Fermi level would *increase* in intensity by a similar factor as the temperature is lowered. The feature at  $245\text{ cm}^{-1}$  cannot be fitted to model a transition between states near the Fermi level.

The optical properties of  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$  are clearly non-Drude type, unlike many disordered metals that may be described by a Drude model in the strong-scattering limit [16]. The striking depression of the optical conductivity at low frequencies suggests either localized electron wave functions, or extended wave functions with unusual band structure. A pseudogap in the density of states has been suggested from band-structure calculations on crystalline approximants [13]. The resulting low density of states at the Fermi surface would lead to suppressed conductivity at low frequencies. However, the conductivity depends not only on the density of states but also on the transition matrix elements which can also lead to a frequency dependence.

For localized states, a mechanism widely used to discuss the frequency-dependent conductivity in the presence of a large amount of disorder is the resonant phononless absorption [17] by singly occupied pairs as a result of an electron transition from the center of one localized state to another. At low temperature for  $\hbar\omega \gg k_B T$  this conductivity is [6,18]

$$\sigma_{\text{ra}}(\omega) = \frac{1}{3} \pi^2 e^2 g_0^2 \omega^2 a r_\omega^4 [\tanh(\hbar\omega/2k_B T)], \quad (1)$$

where  $g_0$  is the density of states at the Fermi surface,  $a$  is the localization length,  $r_\omega = a \ln(2I_0/\hbar\omega)$  is a transition length scale, and  $I_0$  is a model-dependent parameter of the localized states. Equation (1) yields an approximately linear dependence for the conductivity in the region from  $\hbar\omega \approx 0.01I_0$  to  $0.05I_0$ . This linear behavior has also been observed in heavily doped semiconductors [19].

The linear increase of the conductivity with frequency observed here suggests that the dc conductivity, too, would have a component that varies linearly with temperature. The optical conductivity at room temperature, from the least-squares fit, has a slope of  $0.69\text{ }\Omega^{-1}$  or  $0.48\text{ }\Omega^{-1}\text{ cm}^{-1}\text{ K}^{-1}$ . The slope of the dc conductivity is  $0.67\text{ }\Omega^{-1}\text{ cm}^{-1}\text{ K}^{-1}$ , suggesting that most of the temperature dependence of the dc conductivity is due to the same process, activated thermally, that gives rise to the optical conductivity.

In summary, we have presented data for the frequency-dependent conductivity of the stable quasicrystal  $\text{Al}_{63.5}\text{Cu}_{24.5}\text{Fe}_{12}$ . The conductivity follows a unique law: a linear dependence on frequency, a characteristic, we suggest, of marginally metallic conductivity, a boundary separating systems with a gap from systems with a finite dc conductivity.

Models of quasicrystals exist that predict an infinite set of gaps of various sizes separated by continuous regions in the density of states [20]. Within the noise level of our data no structure in the optical conductivity is seen in our samples. Possibly with larger crystals of higher perfection such structure may be resolvable.

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