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Electrodynamic response of Rb_3C_{60}

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The electrodynamic response of Rb_3C_{60} was measured over a broad spectral range. We identify various features in the excitation spectrum of the normal state: a Drude contribution, a mid-infrared absorption, and several interband transitions.

The discovery of superconductivity[1,2] in compounds of C_{60} with alkaline metals at relatively high temperatures created considerable interest. The properties and the parameters, which characterize the superconducting state of the alkali-metal-doped M_3C_{60} compounds, have been explored in detail,[3] however the normal-state properties of these materials are less understood. Band-structure calculations[4] lead to a relatively high density of states at the Fermi level, ϵ_F, while photoemission experiments[5] indicate the development of a pseudogap in the density of states. The magnetic susceptibility and nuclear magnetic relaxation rate[6] indicate a Fermi-liquid behavior. The density of states inferred from these experiments is somewhat larger than that obtained from band-structure calculations and photoemission. Whether this is due to experimental uncertainties or due to an enhancement of the magnetic properties due to electron-electron interactions remains to be seen. The transport properties measured on films do not show typical metallic behavior,[7] and the resistivity increases with decreasing temperature. It is not clear if this is the intrinsic property of the materials or is due to granularity of the films.

Reflectivity measurements have been reported only in the far infrared (FIR) range (i.e., between 20 and 300 cm^{-1}),[8] and the information extracted from the data is the single-particle gap of the superconducting state. In this paper, we report on optical investigations on the complete excitation spectrum of Rb_3C_{60}, and we focus on the normal-state properties. Particularly, we will link the experimental parameters arrived at by our optical investigations to the issues raised above.

The Rb_3C_{60} compounds were prepared from solid-phase reaction of C_{60} powder and alkali vapor in a way similar to that reported earlier.[2] The samples used in the present work were prepared from starting composition of $Rb_{2.8}C_{60}$ heated in vacuum at 200 °C for one week, and subsequently annealed under He atmosphere over several days at the same temperature. X-ray diffraction experiments demonstrated the single crystalline phase nature of our powder samples. The procedure led to a fractional shielding diamagnetism of approximately 30% on powder, determined relative to a Nb bulk reference sample. The small fraction is most probably due to the fine powder used. The samples have a superconducting phase transition temperature $T_c = 29$ K. The powder was then pressed in a He chamber in order to obtain a pellet of about 3 mm diameter and 1 mm thick and sealed in a glass capillary at He atmosphere.

Reflectivity measurements $[R(\omega)]$ were performed between 14 and 50 000 cm^{-1} using three different spectrometers. In the FIR we measured $R(\omega)$ also as function of the temperature. The photon energy range between 14 and 800 cm^{-1} was covered with a Bruker IFS 113v Fourier interferometer with a Hg arc-light source and a He-cooled silicon bolometer detector. From the FIR up to mid-IR a fast-scanning Bruker interferometer IFS 48PC was used, while in the visible spectral range a homemade spectrometer based on a Zeiss monochromator was employed. A gold mirror was used as reference in the FIR and mid-IR. Moreover, after all measurements were performed, we covered our pellets with a 1000-Å layer of gold in order to take into account the surface roughness (particularly important here, since the pellet cannot be polished). No smoothing of the spectra was performed, since the signal-to-noise ratio of the raw data was already very good.

Since the materials are highly air sensitive, precautions and care must be taken in order to measure the compounds in an oxygen-free environment. The samples previously sealed in the He-gas atmosphere capillary were mounted on the sample holder of the different spectrometers in a He-gas glove box. The measurements in various spectrometers were performed in vacuum or He-gas atmosphere conditions, so that the samples were never exposed to air contamination.

Figure 1 shows the $R(\omega)$ spectra on Rb_3C_{60} at 300 and 40 K on the entire energy spectral range investigated. These $R(\omega)$ spectra extending over four decades are subsequently used for Kramers-Kronig (KK) transformation. The frequency range of the measured reflectivity spectrum has been extrapolated towards zero frequency by means of the Hagen-Rubens relation at 40 and 300 K using the ρ_{dc} data published by Palstra *et al.* on K_3C_{60} films,[7] and for energies larger than 50 000 cm^{-1} [where $R(\omega)$ is already approaching zero] the reflectivity has been assumed to drop off as ω^2. The used extrapolation is unique and has no influence on the nearby feature at 35 000 cm^{-1} in the KK-obtained optical conductivity (see below).

Figure 2 displays the optical conductivity $\sigma_1(\omega)$ at 300 K obtained from our KK analysis. We first note, that $\sigma_1(\omega)$, as shown in Fig. 2, is remarkably different from that of a simple metal where the Drude model is appropriate and for which

$$\int_0^\infty \sigma_1(\omega)d\omega=\frac{\pi n e^2}{2m_b} \qquad (1)$$

with n the number of carriers and m_b the band mass. Instead, we observe a Drude-like response—which, however, does not lead to the oscillator strength as given by Eq. (1)—together with a mid-infrared absorption, and several absorptions at higher frequencies due most probably to interband transitions. We first note that the overall behavior of $\sigma_1(\omega)$ is similar to that observed in various correlated materials with low electron density, notably the high-T_c oxides,[9] $BaBi_xPb_{1-x}O_3$,[10] and certain organic conductors.[11] Several mechanisms, based on electron-electron or electron-phonon interactions were suggested in order to explain the behavior of $\sigma_1(\omega)$ (for a review see Ref. 9) in these materials.

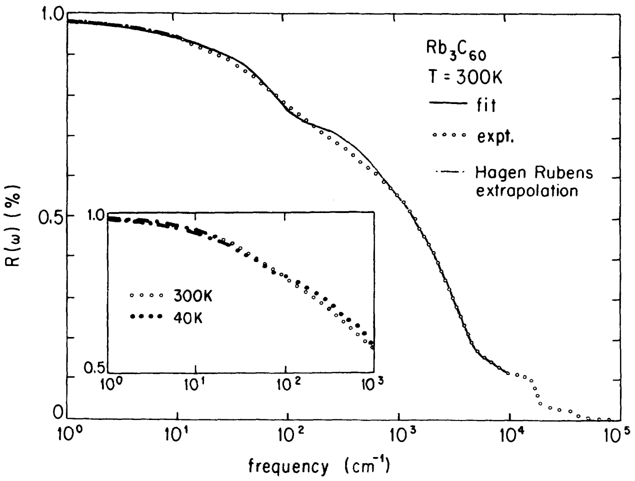

FIG. 1. Reflectivity spectrum at 300 K. The inset displays $R(\omega)$ at 300 and 40 K from the FIR up to the mid-IR. The phenomenological fit, based on Eq. (2), is discussed in the text. The dot-dashed line shows the Hagen-Rubens extrapolation at 300 K.

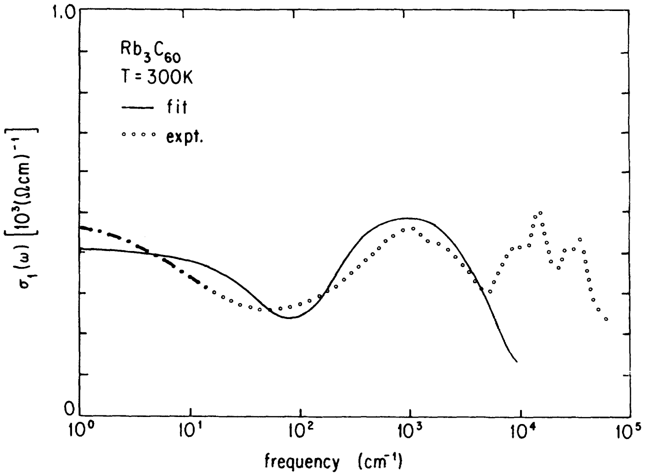

FIG. 2. Optical conductivity at 300 K as evaluated from KK analysis. The phenonenological fit, based on Eq. (2), is discussed in the text. The dot-dashed line shows the KK result in the range of the Hagen-Rubens extrapolation.

Next, we discuss the essential features of our experimental results and compare our findings with band-structure calculations and with parameters extracted from other experiments. At high frequencies (i.e., from the visible to the uv) our excitation spectrum is characterized by broad transitions peaked at 18 000 cm^{-1} (with a shoulder at approximately 10 000 cm^{-1}) and at 35 000 cm^{-1} (also with a shoulder at 30 000 cm^{-1}). We ascribe these excitations to the interband transitions involving *s* and *p* carbon orbitals and *s*, *p*, and *d* alkali orbitals. We remark that our preliminary measurements on the undoped C_{60} are suggestive of interband transitions with different energy positions and oscillator strengths. Our measured conductivity or, correspondingly, the imaginary part of the dielectric function $[\epsilon_2(\omega)]$ of Rb_3C_{60} is in good agreement with the theoretical predictions extracted from a band-structure calculation,[4] which lead to broad peaks centered at 1, 2.5, and 4 eV [see Fig. 3(b) of Ref. 4]. This calculation also suggests that the electronic structure of the ternary alkali-metal-doped C_{60} compounds cannot be simply interpreted as the filling of the extra electrons in the lowest unoccupied conduction bands in the context of a rigid-band model. This has important consequences for the states very close to ϵ_F, as we will discuss below in detail. The theory[4] also predicts weak optical electronic transitions (seen by energy-loss spectroscopy[12]) above 4.5 eV ($\sim$40 000 cm^{-1}), which, however, we do not observe, presumably due to the very low reflectivity in this frequency range.

The low-frequency part of $\sigma_1(\omega)$ (i.e., from FIR up to mid-IR) is characterized by two main features: the broad band centered at approximately 1000 cm^{-1} and the Drude-like contribution to $\sigma_1(\omega)$ at FIR frequencies. In view of these features we model the dielectric function with the following expression:

$$\epsilon(\nu)=\epsilon_\infty+\nu_p^2\left[\frac{f_G}{\nu_G^2-\nu^2-i\nu\gamma_G}-\frac{1-f_G}{\nu(\nu+i\gamma_D)}\right], \quad (2)$$

where ϵ_∞ describes the high-frequency contribution to the dielectric function, while the second and third term in the parentheses describe the mid-IR broad excitation (i.e., at $\sim 1000\ \mathrm{cm}^{-1}$) and the Drude-like response at low frequencies, respectively. The best fit is obtained with the following parameters: $\epsilon_\infty=7$, $\nu_p=13\,471\ \mathrm{cm}^{-1}$, $\nu_G=1000\ \mathrm{cm}^{-1}$, $\gamma_G=6000\ \mathrm{cm}^{-1}$, $\gamma_D=60\ \mathrm{cm}^{-1}$, and $f_G=0.992$. We note, that a frequency-dependent relaxation rate would improve the agreement between $\sigma_1(\omega)$ and the Drude part of the fit in the FIR. This would, however, introduce new parameters, the discussion of which will be far beyond the phenomenological nature of our approach.

Starting with formula (2), there are two main directions that can be followed to interpret our spectroscopic data. The first one, which we will call the one-component picture, is based on the assumption that the low-frequency Drude-like behavior and the harmonic oscillator at 1000 cm^{-1} are due to the response of the conduction band, and, crudely speaking, the charge carriers (which from simple counting arguments have a density $n=4.1\times10^{21}$ cm^{-3}) behave as free carriers at low frequencies and as bound ones at high frequencies. This interpretation is similar to that often applied to the high-T_c Cu-O superconductors and some heavy fermion materials, where a simple Drude model also cannot describe $\sigma_1(\omega)$.[9] Frequency-dependent mass renormalization due to electron-electron interactions, and alternatively midgap states (like polarons or excitons) or a broad phonon spectrum (i.e., Holstein process) were suggested as a source of the frequency-dependent scattering at FIR and mid-IR frequencies. The total spectral weight associated with the plasma frequency $\nu_p=13\,471\ \mathrm{cm}^{-1}$ would correspond to an effective band mass $m_b=2m_e$ with $n=4.1\times10^{21}$ cm^{-3}. This value is somewhat smaller than the value arrived at from spin susceptibility measurements, $m_b=6.5m_e$.[6] From the plasma frequency we calculate a London penetration depth $\lambda_L=c/\omega_p=1200$ Å (appropriate in the clean limit), somewhat smaller than the measured value[6] and in broad agreement with the theoretical value of 1600 Å of Erwin-Pickett.[13]

The second way to interpret Eq. (2) is to consider the two contributions independently, using a two-component picture. Then, the Drude part is characterized by a plasma frequency of $\nu_p=1205\ \mathrm{cm}^{-1}$ [i.e., $(1-f_G)^{1/2}\nu_p$], and the harmonic oscillator is viewed as a separate mid-IR excitation, in a fashion similar to the normal-state description currently used for the high-T_c superconductors.[9] First, we note that the scattering rate (γ_D) of the Drude component is smaller than the superconducting gap 2Δ as evaluated from tunneling spectroscopy measurements[14] ($100\ \mathrm{cm}^{-1}$) and comparable to the value of 2Δ from nuclear magnetic resonance experiments.[15] This suggests that the $\mathrm{Rb_3C_{60}}$ compound is in the clean or nearly clean limit. Our experiments also give a γ_D, which is practically temperature independent above T_c [in agreement with the weak temperature dependence of ρ_{dc} (Ref. 7)]. Of course, the relaxation rate may also be dominated by intergrain scattering. Thus, because of the granularity (see below), our measured $1/\gamma_D$ is a lower limit for the relaxation rate, and in single crystals a larger $\tau\sim1/\gamma_D$ is expected. Nevertheless, we can use our estimation of $1/\gamma_D$ to evaluate the mean free path (l). With the Fermi velocity $v_F=5\times10^6$ cm/sec[6] and the expression $l=v_F\tau$ we obtain $l=45$ Å, which is larger than the coherence length ζ,[6,7] suggesting again that the clean limit is appropriate to describe the superconducting state properties. This conclusion is different from the approach advocated by the Bell group.[7]

We suggest that the broad excitation at approximately 1000 cm^{-1} can be assigned to an electronic interband transition. This interpretation is particularly compelling in view of a recent result obtained with photoemission (XPS) and bremsstrahlung isochromat (inverse photoemission) (BIS) spectroscopy.[5] These experiments indicate that alkali-metal-doping causes a transfer of electronic states from the lowest unoccupied molecular-orbital (t_{1u}) band to an additional band produced in the band gap (of the pure $\mathrm{C_{60}}$). A comparison of the XPS and BIS spectra indicates that a pseudogap of about 0.5 eV ($\sim4000\ \mathrm{cm}^{-1}$) opens at the Fermi level. Thus, our broad excitation peak around 0.1 eV may be considered as the optical evidence of such a pseudogap, and this interpretation would also agree with our observation of a small oscillator strength in the Drude term ($\nu_p=1205$ cm^{-1}). Nevertheless, there are some severe problems also with this two-component picture. In fact, the small plasma frequency associated with the Drude response of the free charge carriers would imply a large effective band mass or a smaller effective number of carriers ($n_{\mathrm{eff}}<n=4.1\times10^{21}\ \mathrm{cm}^{-3}$), and moreover a very large penetration depth compared to the experimental one.[6]

The occurrence of a pseudogap in the density of states of correlated materials is not new, as envisaged, e.g., for $\mathrm{BaBi_xPb_{1-x}O_3}$ [with $x=0.3$ and superconducting transition at $T_c=12$ K (Ref. 16)]. As mentioned earlier, the electrodynamic response as well as the dc transport properties of $\mathrm{Rb_3C_{60}}$ look similar to the results obtain on the Ba-Bi-Pb-O compound,[10,16] and the optical properties of the latter compound were also described with the phenomenological approach based on Eq. (2).[10]

Finally, we address the question of possible granularity in the samples, and its effect on the conclusions given above. We believe that the effect of compressed powder is to lead to a decreased relaxation rate (and correspondingly to an increased dc resistivity). The dc resistivity data can be interpreted in terms of the granularity, which also leads to zero-dimensional superconductivity with an effective grain size of about 70 Å.[7] However, the total oscillator strength is not expected to be strongly modified by granularity, and consequently our conclusions still apply. The same is true for the high-energy part of the spectrum, and the granular nature should not affect the mid-IR absorption and the interband transitions. Consequently, we believe that the essential features of our experimental findings will not be modified when experiment on single crystalline specimens becomes available.

In conclusion, we have reported on our optical investigations on the alkali-metal-doped C_{60} superconductors. We have discussed the high-frequency part of the excitation spectrum in terms of interband transitions. Those excitations were found to be in agreement with high-energy electron spectroscopy results and band-structure calculation as well.[4,5,12] At lower frequencies, we have observed a Drude contribution and a fairly broad excitation in the mid-IR, which we identify as the interband transition, probably related to the so-called pseudogap at the Fermi level as evaluated from XPS and BIS experiments.[5]

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