Optical Response of the Superconducting State of K_3C_{60} and Rb_3C_{60}

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We have measured the optical reflectivity of single phase K_3C_{60} and Rb_3C_{60} compounds, and have evaluated the optical conductivity both below and above the superconducting transition temperature. Our results are in full agreement with a BCS singlet ground state, with the measured gap values consistent with the weak-coupling limit.

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The recent discovery [1] of superconductivity at relatively high temperatures in the alkali-metal C_{60} compounds has created considerable interest. While a variety of experiments on the superconducting state properties, most notably the measurement of the temperature dependence of the penetration depth [2], suggest singlet pairing, the nature of the pairing mechanism is unclear. It has been suggested [3] that electron-electron interactions on the C_{60} balls mediate the pairing. Electron-phonon interactions, involving high-frequency, intramolecular vibrations [4], the alkali-metal counter ions [5], or low-frequency, intermolecular vibrations have also been proposed to be responsible for the superconducting ground state. The energy scale of the various modes which mediate the coupling are different, and therefore, which of these are important could in principle be decided by examining whether the weak- or strong-coupling limit applies. In the case of high-frequency phonons, for example, one expects weak-coupling BCS theory to be appropriate with the ratio of the single-particle gap Δ and the transition temperature T_c given by $2\Delta/k_BT_c=3.52$. In the case of low-frequency vibrations, on the other hand, $2\Delta/k_BT_c$ is expected to exceed the value which is appropriate for the weak-coupling limit.

Available experiments lead to different values of the single-particle gap in K_3C_{60} and Rb_3C_{60} compounds. Tunneling measurements [6] on both compounds place the single-particle gap well into the strong-coupling limit with $2\Delta/k_BT_c\approx 5$. Optical experiments either claim to observe the weak-coupling limit [7] or to reflect a distribution of superconducting gaps [8]. The reasons for these differences are not understood at present. However, one should remark that tunneling experiments, because of the extreme air sensitivity of these materials, may be subject to surface effects with Δ different in the surface layers than in the bulk. On the other hand, optical data, which are based only on the ratio of the normal and superconducting state reflectivities R_s/R_n or transmissions T_s/T_n as have been done by Rotter *et al.* [7] and Fitzgerald *et al.* [8], respectively, show that the resulting gap depends on several assumptions about the superconducting state. In fact, the ratio of the superconducting to normal transmittance, e.g., was interpreted assuming a distribution of gaps (or equivalently of materials with different T_c) within an effective-medium approximation [8]. This might be valid especially for materials, such as granular metals, when normal and superconducting regions coexist [9]—a situation not unlikely in alkali-doped C_{60} specimens, which might not be of single phase or where doping is inhomogeneous.

In the Letter we report (absolute) optical reflectivity measurements on single-phase K_3C_{60} and Rb_3C_{60} specimens, prepared in a pressed pellet form. Our reflectivity measurements show clear evidence of well-defined superconducting gaps with $2\Delta/k_BT_c$ in full agreement with the prediction of the weak-coupling BCS limit. Furthermore, the measured conductivity can be described by the Mattis-Bardeen [10] formalism of the electrodynamic response. The implications of these results are also discussed.

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 [1]. The samples used in the present work were prepared from a starting composition of $Rb_{2.8}C_{60}$ and K_4C_{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 between 15% and 30% on powder, determined relative to a Nb bulk reference sample. The reduced Meissner fraction is most probably due to the fine powder used with the grain size comparable to the penetration depth. The samples have a superconducting phase transition temperature $T_c=29$ and 19 K for the Rb and K fullerene, respectively. 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 with He atmosphere.

Reflectivity measurements $[R(\omega)]$ were performed between 14 and 50000 cm^{-1} using three different spectrometers. In the far infrared (FIR) spectral range we measured $R(\omega)$ also as a 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 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 a reference in the FIR and mid IR. After all measurements, the pellets were covered with a 400-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 has been performed, since the signal-to-noise ratio of the raw data was adequate.

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 under He gas atmosphere in a capillary were mounted on the sample holder of the different spectrometers in a He gas glove box. The sample holders are so designed to allow an oxygen-free transportation of the samples from the gas glove box within the spectrometers. This allows furthermore a complete removal of the capillary (where the samples were sealed) for the optical investigations. The measurements in various spectrometers were then performed in vacuum or He gas atmosphere conditions, so that the samples were never exposed to air contamination.

In Fig. 1, we display the optical reflectivity measured both above and below the superconducting transition temperature, in the spectral range which covers the (expected) superconducting gap values. In the normal state the behavior for both compounds is the same and for K_3C_{60} is similar to what has been reported by us earlier on Rb_3C_{60} [11]. We observe a low-frequency Drude behavior together with a midinfrared absorption band; this characteristic is similar to that found in several oxide superconductors in their normal state [11]. At low frequencies, the reflectivity is well described by the so-called Hagen-Rubens limit (see dashed-double-dotted line in Fig. 1). The optical reflectivity below T_c shows a well-defined gap feature, which becomes progressively sharper when the temperature is decreased. However, the gap feature does not decrease remarkably by raising the temperature from 6 K up to T_c, as it would be expected according to a simple BCS picture. While this particular temperature dependence of the reflectivity below T_c is similar to what has been found by the previously mentioned investigations [7,8], it still remains to be seen whether it is an indication of measurement uncertainty [although the behavior of $R(\omega)$ below T_c appears to be outside the experimental error] or the consequence of an intrinsic physical mechanism (like, e.g., a gap distribution [8]).

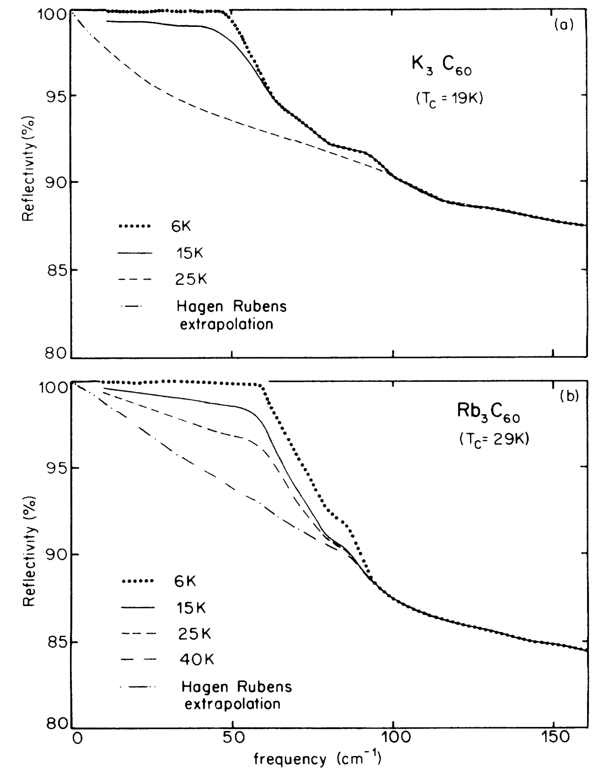

FIG. 1. Optical reflectivity at several temperatures in the infrared spectral range for (a) K_3C_{60} and (b) Rb_3C_{60}.

Although not shown, reflectivity measurements were conducted up to 10^5 cm^{-1}, and this allows the evaluation of the optical conductivity by using the Kramers-Kronig analysis [11]. The resulting conductivity $\sigma_1(\omega)$ is, in the infrared spectral range, insensitive to the high-frequency extrapolation procedure [11]. The frequency-dependent conductivity $\sigma_1(\omega)$ measured for both compounds above T_c and well below T_c is displayed in Fig. 2. The low-frequency extrapolation of $\sigma_1(\omega)$ (dashed-double-dotted line) is that of the Hagen-Rubens form in the normal state, and this leads to a dc conductivity $\sigma = ne^2\tau/m$ of 1.2×10^3 $(\Omega\ cm)^{-1}$ and 1.3×10^3 $(\Omega cm)^{-1}$ for Rb_3C_{60} and K_3C_{60}, respectively, in full agreement with the dc [12,13], or microwave [14], resistivity values. In the superconducting state at $T=6$ K, our reflectivity data are, up to a well-defined threshold frequency of 48 cm^{-1} for K_3C_{60} and 60 cm^{-1} for Rb_3C_{60} (see Fig. 1), within the experimental error of 0.5% equal to 100%, and we have used this value to evaluate the optical conductivity. This procedure gives, for both compounds zero conductivity up to a threshold frequency which we identify as the superconducting gaps and we obtain $\Delta = 24$ cm^{-1} for the K and 30 cm^{-1} for the Rb compound. Together with the superconducting transition temperatures $T_c = 19$ and 29

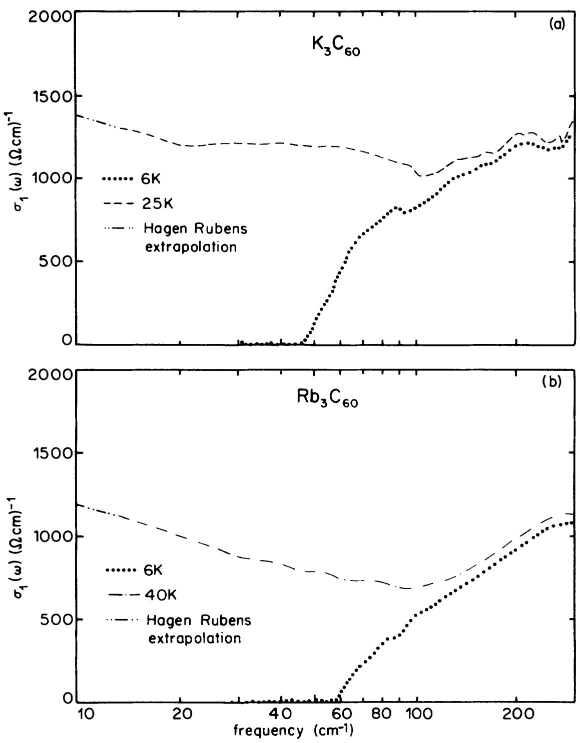

FIG. 2. The optical conductivity above and below T_c for (a) K_3C_{60} and (b) Rb_3C_{60}, evaluated from the reflectivity data of Fig. 1 (note the logarithmic frequency scale).

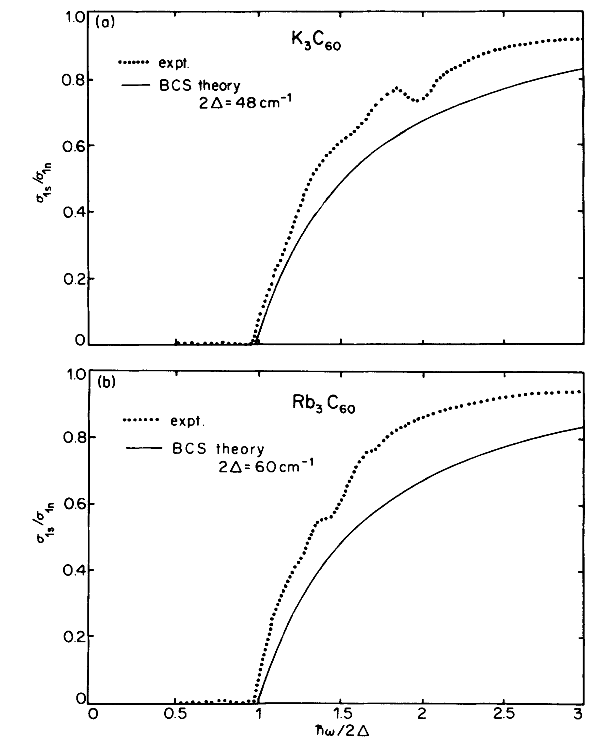

FIG. 3. The measured optical conductivity together with $\sigma_1(\omega)$ calculated using the Mattis-Bardeen theory (BCS) with the single-particle gap values given in the text.

K this leads to the ratio $2\Delta/k_BT_c=3.6$ and 2.98 for K_3C_{60} and Rb_3C_{60}, with both values in good agreement with the weak-coupling BCS result of $2\Delta/k_BT_c=3.52$. Our conductivity results, evaluated as discussed above, can be compared with the measured [2,15] penetration-depth values using the missing spectral weight argument [16]. The penetration depth λ is given by

$$\lambda^2=\frac{c^2}{8A},\quad A=\int_0^\infty[\sigma_{1,n}(\omega)-\sigma_{1,s}(\omega)]d\omega\,, \tag{1}$$

where c is the speed of light, and $\sigma_{1,n}$ and $\sigma_{1,s}$ are the optical conductivity in the normal and superconducting state, respectively. We performed the integral A up to the frequency ω where $\sigma_{1,n}$ and $\sigma_{1,s}$ are no longer different within the experimental error of our measurement [17], and we obtain $\lambda=8000\pm500$ Å for the two compounds, in satisfactory agreement with the penetration depth of 6000 Å [18] or 4800 Å [2] for K_3C_{60}, and 4600 Å [18] or 4200 Å [15] for Rb_3C_{60}.

The functional form of $\sigma_1(\omega)$ at frequencies above the gap frequency has been evaluated first by Mattis and Bardeen [10], and this theory leads to

$$\frac{\sigma_{1s}}{\sigma_{1n}}=\left(1+\frac{2\Delta}{\hbar\omega}\right)E(k)-\frac{4\Delta}{\hbar\omega}K(k)\,, \tag{2}$$

where $k=(\hbar\omega-2\Delta)/(\hbar\omega+2\Delta)$, and $E(k)$ and $K(k)$ are the tabulated complete elleptic integrals. The functional form is dependent only on the gap frequency. Equation (2), together with the measured optical conductivity, is displayed for both compounds in Fig. 3. Given the fact that the calculation neglects the role played by mean free path effects, the agreement between our results and the theory based on a BCS ground state is excellent. We also note that the functional form also reflects the so-called case II coherence factors [16] which depend sensitively on the symmetry of the superconducting wave function, and therefore the agreement between theory and experiment gives clear evidence for a singlet ground state.

The observation of a well-defined superconducting gap would suggest that, strictly speaking these materials are not in the so-called clean limit, where the mean free path l exceeds the coherence length ζ. This issue has been addressed before [12,13,19] and is the subject of acute controversy. The question of whether the clean or the dirty limit applies is based on the assumption that a simple Drude response accounts for the conductivity in the metallic state. We have shown before [11], and it is also evident from Fig. 2, that $\sigma_1(\omega)$ cannot be described by the Drude model alone, but can be accounted for by a low-frequency Drude response and a midinfrared absorption. Both features contribute, within the one component picture of the normal state [11], to the total spectral weight

$$\int_0^{\omega_c} \sigma_1(\omega) d\omega = \frac{ne^2}{m_b} = \frac{\omega_p^2}{8}, \qquad (3)$$

with n the number of carriers, m_b the band mass, and ω_c a cutoff frequency (i.e., of the order of 10^4 cm^{-1}, chosen so as to include contributions from the band which intersects the Fermi level, but excluding the high-lying bands). Therefore, in order to evaluate the various parameters of the superconducting state such as the London penetration depth, or the coherence length in terms of the normal state properties (given in the Drude model by the single parameter l, or equivalently τ), a more elaborate analysis is necessary.

In conclusion, we have examined the electrodynamic response of the superconducting ground state in K_3C_{60} and Rb_3C_{60}. The measured optical conductivity is in full agreement with that of a BCS singlet superconductor, and the magnitude of the single-particle gaps also agree with the weak-coupling limit. This would suggest that the relevant excitation responsible for superconductivity pairing is significantly larger than the energy associated with the single-particle gap in these materials.

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[1] A. F. Hebbard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature (London) **350**, 320 (1991); K. Holczer, O. Klein, S.-M. Huang, R. B. Kaner, K.-J. Fu, R. L. Whetten, and F. N. Diederich, Science **252**, 600 (1991).

[2] Y. J. Uemura, A. Keren, L. P. Le, G. M. Luke, B. J. Sternlieb, W. D. Wu, J. H. Brewer, R. L. Whetten, S.-M. Huang, S. Liu, R. B. Kaner, F. Diederich, S. Donovan, G. Grüner, and K. Holczer, Nature (London) **352**, 605 (1991).

[3] S. Chakraverty and S. Kivelson, Europhys. Lett. **16**, 751 (1991).

[4] C. M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991); M. Schluter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tomanek, Phys. Rev. Lett. **68**, 526 (1992).

[5] F. C. Zhang, M. Ogata, and T. M. Rice, Phys. Rev. Lett. **67**, 3452 (1991).

[6] Z. Zhang, C.-C. Chen, S. P. Kelty, H. Dai, and C. M. Lieber, Nature (London) **353**, 333 (1991).

[7] L. D. Rotter, Z. Schlesinger, J. P. Cauley, N. Courtel, J. E. Fischer, and A. B. Smith, Nature (London) **355**, 532 (1992).

[8] S. A. Fitzgerald, S. C. Kaplan, A. Rosenberg, A. J. Sievers, and R. A. S. McMordie, Phys. Rev. B **45**, 10165 (1992).

[9] See, for example, T. W. Noh, P. H. Song, and A. J. Sievers, Phys. Rev. B **44**, 5459 (1991), and references cited therein.

[10] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

[11] L. Degiorgi, G. Grüner, P. Wachter, S.-M. Huang, J. Wiley, R. L. Whetten, R. B. Kaner, K. Holczer, and F. Diederich, Phys. Rev. B **46**, 11250 (1992).

[12] T. T. M. Palstra, R. C. Haddon, A. F. Hebbard, and J. Zaanen, Phys. Rev. Lett. **68**, 1054 (1991).

[13] X. D. Xiang, J. G. Hou, G. Briceno, W. A. Vareka, R. Mostovoy, A. Zettl, V. H. Crespi, and M. L. Cohen, Science **256**, 1190 (1992).

[14] O. Klein, G. Grüner, S.-M. Huang, J. B. Wiley, and R. B. Kaner, Phys. Rev. B **46**, 11247 (1992).

[15] Y. T. Uemura, L. P. Le, and G. M. Luke, in Proceedings of the International Conference on Science and Technology of Synthetic Metals, Göteborg, Sweden, 1992 [Synth. Met. (to be published)].

[16] See, for example, M. Tinkham, in *Introduction to Superconductivity*, edited by R. E. Krieger (Krieger, Malabar, FL, 1975).

[17] This frequency is $\omega = 350$ cm^{-1} for K_3C_{60} and for Rb_3C_{60}.

[18] R. Tycko, G. Dabbagh, M. J. Rosseinsky, D. W. Murphy, A. P. Ramirez, and R. M. Fleming, Phys. Rev. Lett. **68**, 1912 (1992).

[19] G. Sparn, J. D. Thompson, R. L. Whetten, S.-M. Huang, R. B. Kaner, F. Diederich, G. Grüner, and K. Holczer, Phys. Rev. Lett. **68**, 1228 (1992); K. Holczer, O. Klein, G. Grüner, J. D. Thompson, F. Diederich, and R. L. Whetten, Phys. Rev. Lett. **67**, 271 (1991).