

## Optical measurements of the superconducting gap in single-crystal $K_3C_{60}$ and $Rb_3C_{60}$

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THE mechanism of superconductivity in alkali-metal compounds of  $C_{60}$  (refs 1, 2) remains controversial. Electron-pairing mechanisms based on electron-phonon coupling involving both low-frequency (intermolecular) vibrations<sup>3</sup> and high-frequency (intramolecular) modes<sup>4,5</sup>—the strong-coupling and weak-coupling cases respectively—have been proposed. These two mechanisms have different associated energy scales, which is reflected in the magnitude of the superconducting energy gap. Measurements of the gap for these compounds have been reported previously for powder samples<sup>6–8</sup>, but are somewhat discrepant or ambiguous, perhaps owing to grain-size or grain-junction effects. Here we report measurements on large single-crystal samples of  $K_3C_{60}$  and  $Rb_3C_{60}$  using optical reflectivity. We obtain values for the reduced gap ratio,  $2\Delta/k_B T_c$ , of 3.44 and 3.45 respectively, consistent with predictions for a mechanism based on standard Bardeen-Cooper-Schrieffer (BCS) electron-phonon coupling to intramolecular modes.

High-quality single crystals of  $K_3C_{60}$  and  $Rb_3C_{60}$  were prepared by doping vapour-transport-grown  $C_{60}$  crystals with alkali metals. The synthesis follows a method similar to that described previously<sup>9,10</sup>. The crystals had a superconducting transition

temperature  $T_c$  of 20.3 and 30.5 K (that is, where the resistivity  $\rho(T_c)=0$  (refs 9, 10)), and had large and shiny surfaces with dimensions  $1.5 \times 2$  mm and  $2 \times 2$  mm for  $K_3C_{60}$  and  $Rb_3C_{60}$ , respectively.

Reflectivity measurements ( $R(\nu)$ ) were performed between 2 meV and 6 eV as a function of temperature using three different spectrometers, with overlapping frequency ranges as described in previous work<sup>8</sup>. The absolute accuracy of the measurement is  $\sim 0.8\%$ , whereas the relative accuracy (important for the temperature dependence of  $R(\nu)$ ) is better than 0.3%.

The reflectivity of  $Rb_3C_{60}$  in the normal state is displayed in Fig. 1 (results for  $K_3C_{60}$  are similar). Besides the overall metallic behaviour (see inset and ref. 8), we recognize in the mid-infrared frequency range two well defined absorptions at 0.07 and 0.17 eV, which are ascribed to the infrared-active  $T_{1u}$  phonon modes<sup>11,12</sup>. These modes were missing in our previous investigation of the pressed-pellet specimens (probably because of the large surface scattering due to the grains)<sup>8</sup>. Their appearance and the fair agreement with the expected frequency of these modes for this alkali-metal doping level (that is,  $A_xC_{60}$  with  $x=3$ )<sup>11,12</sup> are evidence for the very good quality of the samples and the outstanding resolution of these new optical measurements.

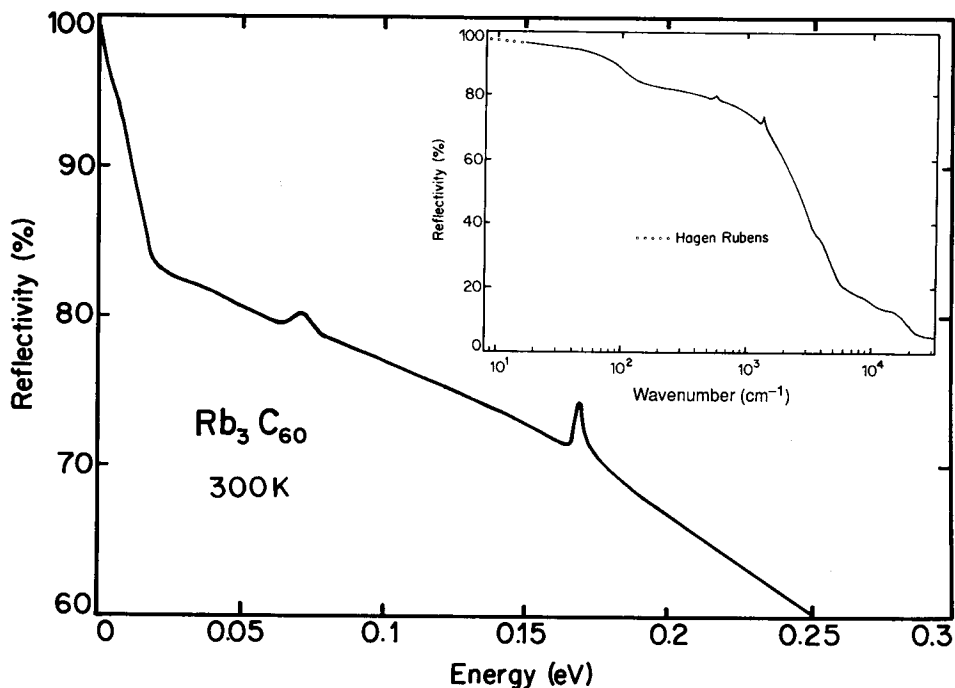
Figure 2 presents the reflectivity spectra in the far-infrared of  $K_3C_{60}$  and  $Rb_3C_{60}$  single crystals. It is clearly seen that below 0.014 eV,  $R(\nu)$  is enhanced and the onset of this BCS-like enhancement is coincident with  $T_c$ . At the lowest temperature ( $\sim 6$  K) the reflectivity is, within experimental error, 100% below a threshold frequency of  $\sim 6$  and 9 meV for  $K_3C_{60}$  and  $Rb_3C_{60}$ , respectively. By performing Kramers-Kronig transformations<sup>8</sup>, we obtain the optical conductivity  $\sigma_1(\nu)$ , which is displayed in Fig. 3 at several temperatures. The optical conductivity at 6 K is zero up to the threshold frequencies indicated above, which we ascribe to the optical identification of the superconducting gap. These values correspond to a reduced gap ratio of  $2\Delta/k_B T_c = 3.44$  and 3.45 for  $K_3C_{60}$  and  $Rb_3C_{60}$ , respectively, which suggests a weak coupling BCS limit. Our earlier measurements<sup>8</sup> on a pressed pellet hinted at this conclusion; but scattering due to grain-size effects may play an important role in polycrystalline samples, reducing or partially smearing out the intrinsic gap value.

The normal-state properties (spectra above  $T_c$  in Fig. 3) deviate considerably from the simple Drude behaviour expected for conventional metals (that is,  $\sigma_1(\nu)$  should be constant in the frequency range of Fig. 3), as discussed in ref. 8. This is due to a broad mid-infrared absorption at  $\sim 60$  meV, which produces a shallow minimum in  $\sigma_1(\nu)$  around 12 meV. The presence of such a mid-infrared absorption might lead to another explanation of the data: that the behaviour of  $R(\nu)$  below  $T_c$  is due to a type of plasma-edge effect<sup>13</sup>. Both the coincidence with  $T_c$  of the onset of the temperature dependence of  $R(\nu)$ , and particularly the absence of any zero crossing of the real part of the dielectric function  $\epsilon_1(\nu)$  (which would define the screened plasma frequency)<sup>13</sup> in the far-infrared frequency range, clearly rule out this explanation.

The experimental electrodynamic response is in a fairly good agreement with the Mattis-Bardeen calculation within the BCS framework<sup>14</sup> or, in a more sophisticated way, with the predictions of the standard Eliashberg theory, as discussed previously for polycrystalline specimens<sup>8</sup>. Within the Eliashberg formalism, one considers a realistic phonon spectrum and directly singles out those phonon modes that are relevant for superconductivity. This approach reduces to the weak coupling BCS Mattis-Bardeen calculation in the limit of the average phonon frequency being much greater than  $T_c$ , but impurity scattering effects can also be incorporated. We found that the self-consistent Eliashberg calculation within a phonon model spectrum dominated by high-frequency intramolecular modes gives a reduced gap ratio of  $\sim 3.5$  and moreover reproduces perfectly the experimental dynamical conductivity<sup>8</sup>. On the contrary, an important disagreement is found when low-energy

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FIG. 1 Normal state reflectivity spectrum of  $\text{Rb}_3\text{C}_{60}$  in the mid-infrared frequency range. The inset displays the whole spectrum (note the logarithmic scale). The Hagen Rubens extrapolation of the reflectivity data to zero frequency corresponds to the expression  $R(\nu) = 1 - 2(\nu/\sigma_0)^{1/2}$ , where  $\sigma_0$  is the d.c.-conductivity.



phonon modes are considered; then,  $2\Delta/k_B T_c$  turns out to be of the order of 5. This is consistent with the conclusions of other experiments. The specific-heat isotope effect and the normal-state susceptibility investigations<sup>15,16</sup>, the pressure and temperature dependence of the nuclear spin lattice relaxation<sup>17</sup>, and the muon spin relaxation ( $\mu\text{SR}$ ) experiments<sup>7</sup>, are also strongly indicative that the relevant excitation for the pairing mechanism is related to high-frequency intramolecular phonon modes, thus being consistent with a BCS weak-coupling limit.

Although tunnelling measurements<sup>6</sup> show a BCS-like density of states in the superconducting phase, they indicate a reduced gap ratio ( $2\Delta/k_B T_c$ ) larger than 5, implying a strong-coupling limit. On the other hand, a recent  $\mu\text{SR}$  experiment shows a reduced Hebel-Slichter peak, compared to the BCS prediction<sup>7</sup>. This latter result might indicate a significant broadening in the density of states  $D_s(E)$  in the superconducting phase. However, it remains to be seen whether this discrepancy of the gap ratio could be traced to such a broadening of  $D_s(E)$ .

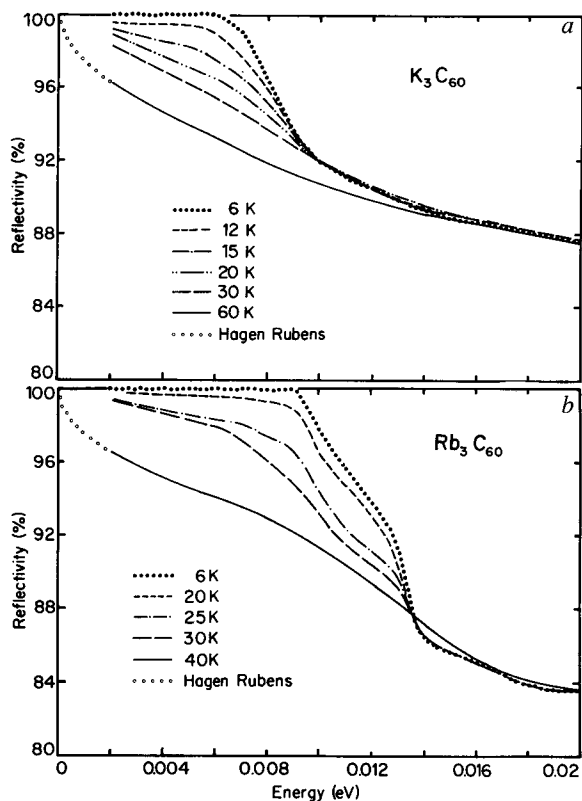


FIG. 2 Far-infrared reflectivity spectra above and below  $T_c$  of  $\text{K}_3\text{C}_{60}$  (a) and  $\text{Rb}_3\text{C}_{60}$  (b).

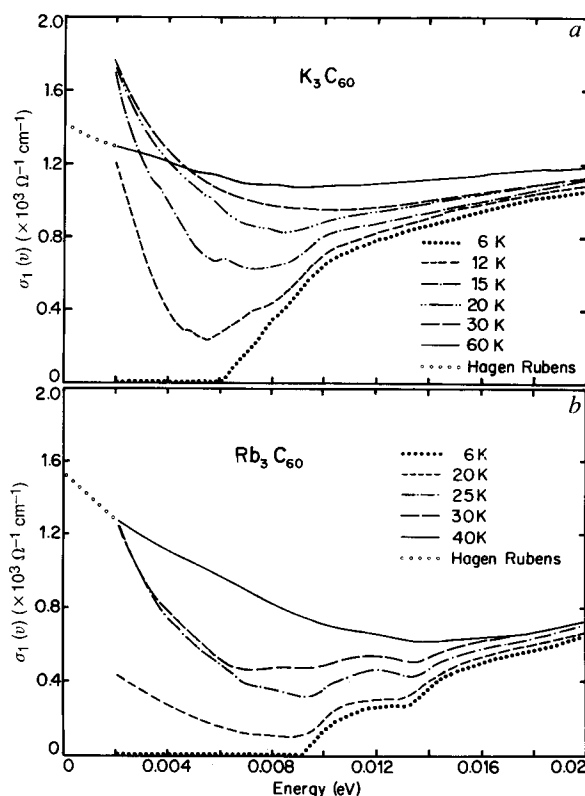


FIG. 3 Optical conductivity in the far-infrared above and below  $T_c$  of  $\text{K}_3\text{C}_{60}$  (a) and  $\text{Rb}_3\text{C}_{60}$  (b).

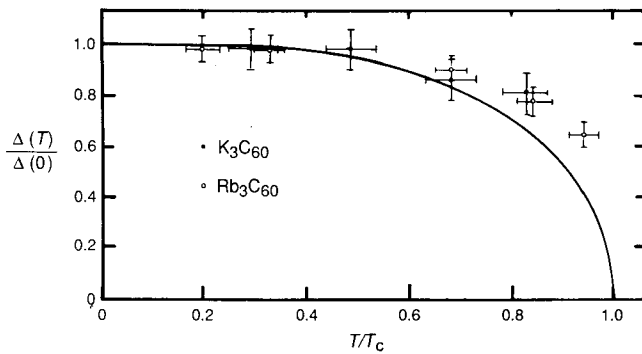


FIG. 4 Temperature dependence of the experimentally obtained superconducting gap (renormalized to  $\Delta(0) = 1.76k_B T_c$ ), compared with the weak-coupling limit of the BCS theory (solid line). The empty and filled circles refer to  $\text{Rb}_3\text{C}_{60}$  and  $\text{K}_3\text{C}_{60}$ , respectively. The error bars correspond to  $\pm 1$  K and  $\pm 0.25$  meV.

Figure 3 also displays the temperature dependence of the optical conductivity from the superconducting ground state up to the normal state. First, we note that the  $\text{K}_3\text{C}_{60}$  data (Fig. 3a) might be also suggestive of the appearance of the so-called coherence peak at low frequencies (below 3 meV). But because this feature is at the very lower end of our experimentally accessible frequency range, at present we consider this possibility very unlikely. The possibility needs to be investigated, however, by further experiments in the frequency range below the far-infrared. Nevertheless, the overall optical conductivity increases with increasing temperature due to the progressively larger amount of free charge carriers excited across the superconducting gap. The temperature dependence of the superconducting gap can be evaluated either by the maximum of the so-called relative reflectivity given by the ratio  $R_s/R_n$  of the reflectivity in the superconducting state over the reflectivity in the normal state, or by fitting the temperature dependence of the experimental ratio  $\sigma_{1s}/\sigma_{1n}$  with the Mattis-Bardeen BCS calculation<sup>14</sup>. Figure 4 shows the temperature dependence of  $\Delta$ , normalized to  $\Delta(0) = 1.76k_B T_c$ , as evaluated from the Mattis-Bardeen approach. While the general trend seems to be suggestive of a BCS-like behaviour, the gap ratio is always enhanced with respect to the BCS prediction as  $T_c$  is approached. Previous optical investigations<sup>8,18,19</sup> also indicated an anomalous temperature independence of  $\Delta$ . Thermal broadening, particularly close to  $T_c$  where a realistic determination of  $\Delta$  is impossible, might be important so that the intrinsic temperature dependence of  $\Delta$  is beyond the precision of the optical measurement<sup>8</sup>. Moreover, a gap distribution, due to a different  $T_c$  (that is, inhomogeneity of the specimens)<sup>18,19</sup> has been also suggested. Such a gap distribution can be, furthermore, the consequence of a gap anisotropy at the Fermi level, so that as the temperature is lowered below the onset of the transition, the regions with large gaps become superconducting first, with regions of smaller gaps following at lower temperatures<sup>18,19</sup>. Alternatively, the temperature dependence of the gap (Fig. 4) might be reminiscent of a fairly broad density of states, as also suggested experimentally by the  $\mu\text{SR}$  investigation<sup>7</sup>. All these effects cause the apparent weak temperature dependence of the gap feature when the temperature is raised towards  $T_c$ . □

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