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Raman studies of electron-phonon interaction in K_xC_{70}

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The Raman spectra of pristine C_{70} films and K_xC_{70} doped to the maximum-conductivity phase (nominally K_4C_{70}) are studied. All the Raman modes for C_{70} are only moderately broadened upon K doping, distinctively different from the superconducting K_3C_{60} where several H_g modes are broadened to the extent that they have almost disappeared from the spectrum. Assuming that the electron-phonon interaction is responsible for the broadening, the electron-phonon coupling strength is found to be comparable to the Coulomb repulsion. These results are important for understanding the absence of superconductivity in K_xC_{70}.

Since the discovery of superconductivity in alkali-metal-doped C_{60}, extensive research on C_{60} and other fullerenes has been carried out worldwide, aimed at understanding the mechanism for superconductivity and other related issues in fullerenes.[1–7] Several theoretical models have been proposed to explain the formation of the superconducting state in K_3C_{60}.[1–5] These theories can be classified into two major categories: those assuming that electron-phonon interaction is important[1–4] and those based on the electron-electron interaction.[5] The electron-phonon interaction theories can be further divided into two branches: interaction of electrons with intramolecular phonons[1–3] and with intermolecular phonons.[4] Although it is still an open question as to which of these theories is the appropriate one for K_3C_{60}, Raman studies of M_3C_{60} (M= K, Rb)[2,3,6,7] favor the intramolecular-phonon-coupling mechanism. Based on the experimentally observed Raman line broadening, the electron-phonon coupling constant λ for M_3C_{60} and hence the superconducting transition temperature T_c have been estimated. The results are consistent with the measured T_c values.[2,3,6,7]

Compared with C_{60}, considerably less attention has been paid to C_{70} and its alkali-metal-doped compounds. The theoretical predictions about the possible superconductivity in K_xC_{70} are contradictory.[5,8] According to a band-structure calculation, formation of a superconducting phase in M_xC_{70} is favorable,[8] whereas the electron-electron interaction theory comes to the opposite conclusion.[5] The electron-phonon models have not yet been applied to the M_xC_{70} system, presumably due to the lack of phonon spectral data. Experimentally, it is found that the doping of C_{70} with alkali metals, say potassium, results in a maximum-conductivity phase,[9] nominally K_4C_{70},[9,10] which is not superconducting at temperatures (T) as low as 1.35 K.[9] Whether or not K_4C_{70} becomes superconducting at even lower T is still an open question, let alone the theoretical understanding of why K_4C_{70} is, or is not, superconducting. Answers to the above questions are very important for understanding the mechanism for superconductivity in fullerenes.

In this paper, we present Raman studies of K_xC_{70} doped to the maximum-conductivity phase. In K_xC_{70}, all the Raman modes are only moderately broadened, as compared with those of C_{70}, contrary to the superconducting K_3C_{60} in which several H_g modes are so broadened that they become nearly invisible in the spectrum.[6,7] The frequency shifts of the modes can be understood in terms of a bond-length change induced by charge transfer[11–15] and a mode-stiffening mechanism proposed by Jishi and Dresselhaus.[12–14] Assuming the broadening is mainly due to the electron-phonon interaction, we estimate below an upper limit of the electron-phonon coupling constant λ of 0.1, which is comparable with the Coulomb repulsion $\mu^* \sim 0.1$–0.2,[1,2] thus ruling out the possibility for superconductivity in K_xC_{70} on the basis of an intramolecular phonon mechanism.

Pristine C_{70} films with thickness of 2500 Å were deposited on a suprasil substrate by thermal sublimation of C_{70} powder (97% pure with C_{60} as the major impurity). Doping C_{70} films with K was carried out in a sealed Pyrex ampoule, with tungsten-wire feed-throughs for attaching leads to the sample to monitor the conductivity. The films were baked overnight at 160–180 °C under a vacuum of 5×10^{-7} torr before sealing. The films, which were maintained at T_s=100–115 °C, were slowly intercalated with K at T_b=90–100 °C over a period of one or two days. Typically, the conductivity σ initially increased to a maximum value of ~15 S/cm. Upon further doping, σ first decreased to a minimum value of ~5 S/cm, but later increased again to another maximum value $\sigma_{\max} \sim 600$ S/cm. (We refer to this phase as the maximum-conductivity phase or K_4C_{70} for convenience.) Further doping is very slow and σ decreases only a few percent over several hours. Increasing T_s above 150 °C, while keeping T_b the same, would cause deintercalation of the films and a relatively low doping level would finally be reached. For the Raman experiments, the Ar^+ laser line at 488 nm is used with a flux of ~ 50 mW/mm^2 incident onto the films sealed inside a Pyrex ampoule. A slit width of 0.3 and 0.4 mm was used for pristine and doped C_{70}, respectively.

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The room-temperature Raman spectra of pristine C_{70} and K_xC_{70} (x ~4) are depicted in Fig. 1. The peak positions and full linewidth at half-maximum intensity (Γ) of the spectral lines are listed in Table I, together with their symmetry classifications. Due to the doping of K, the modes are shifted and broadened. The shifting $\Delta\omega \equiv \omega(K_4C_{70}) - \omega(C_{70})$ and the broadening $\Delta\Gamma \equiv \Gamma(K_4C_{70}) - \Gamma(C_{70})$ are shown in Fig. 2. The mode frequency shifts ($\Delta\omega$) and calculated frequency shifts[13,14] ($\Delta\omega'$) for M_6C_{70} are also listed in Table I.

The T dependence of the resistivity $\rho(T)$ for the K_4C_{70} sample in the T range of 4–300 K is plotted in Fig. 3, together with a theoretical fitting curve calculated according to the fluctuation-induced-tunneling (FIT) model $\rho \propto \exp[T_1/(T+T_0)]$ where T_1 and T_0 are fitting parameters.[9] No superconducting transition was observed in this T range. Measurements on another sample for T as low as 1.35 K still show a finite ρ, ruling out the possibility of a superconducting transition above 1.35 K.[9]

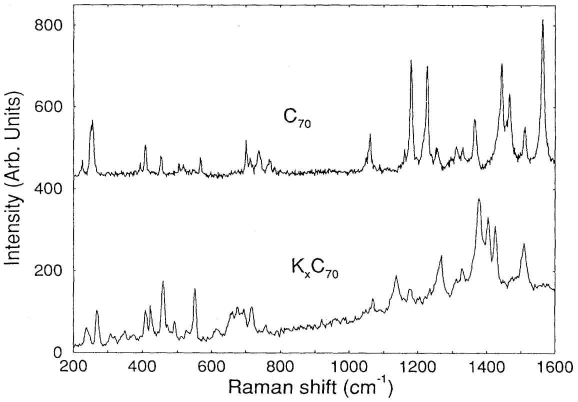

FIG. 1. Room-temperature Raman spectra of pristine C_{70} and K_xC_{70} at the maximum-conductivity phase (nominally $x = 4$). The film thickness is 2500 Å.

TABLE I. Experimental Raman-mode frequencies of C_{70} and K_4C_{70}, the frequency shift $\Delta\omega = \omega(K_4C_{70}) - \omega(C_{70})$, and the corresponding full width at half maximum intensity. The first column lists the symmetry of each Raman line (Refs. 13 and 14). The fifth column gives the calculated frequency shifts for M_6C_{70} [$\Delta\omega' = \omega(M_6C_{70}) - \omega(C_{70})$] using a force-constant model (Refs. 13 and 14). In the last column $\Delta\Gamma \equiv \Gamma(K_4C_{70}) - \Gamma(C_{70})$, after full widths are corrected for the instrumental resolution.

Raman modes (cm^{-1})			Mode shift (cm^{-1})		Full width (cm^{-1})		
Symmetry	C_{70}	K_4C_{70}	$\Delta\omega$	$\Delta\omega'$	C_{70}	K_4C_{70}	$\Delta\Gamma/\omega^2$ (cm)
A_1'	226	239	13	39	4.3	15.0	2.1×10^{-4}
E_2'	256	269	13	−13	12.9	11.4	-2.3×10^{-5}
A_1'	311[a]	321[a]	10	−14	11.4	14.3	3.0×10^{-5}
E_2'	394	409	15	−31	3.7	10.0	4.1×10^{-5}
E_2'	408	423	15	−44	7.6	7.1	-3.0×10^{-6}
A_1',E_1''	454	458	4	−28	6.4	11.3	2.38×10^{-5}
E_2'	489[a]	472[a]	−17	−43	2.8	5.7	1.21×10^{-5}
E_2'	505	482	−23	−52	5.7	7.1	5.5×10^{-6}
A_1'	517	492	−25	−71	7.3	7.1	-7.5×10^{-7}
E_1''	547[a]	527	−20	−41	8.8	13.7	1.64×10^{-5}
E_1''	567	552	−15	−41	6.2	9.7	1.09×10^{-5}
		614					
E_2'	702	659	−43	−71	6.6	20.5	2.82×10^{-5}
E_1''	712	676	−36	−61	9.6	23.9	2.83×10^{-5}
A_1'	737	695	−42	−67	14.0	14.5	9.2×10^{-7}
E_2'	767	717	−50	−48	14.7	13.7	-1.7×10^{-6}
E_1''	783	738	−45	−5	8.5	8.5	0.0
E_2'	1060	1068	8	−12	8.6	6.9	-1.5×10^{-6}
A_1'	1162	1120	−42	−4	5.9	5.5	-3.0×10^{-7}
E_2',E_1''	1181	1136	−45	0	8.6	21.5	9.2×10^{-6}
E_2'	1200[a]	1158[a]	−42	−10			
E_1''	1228	1180	−48	−6	7.4	13.9	4.3×10^{-6}
A_1'	1252	1199[a]	−53	7			
E_2'	1296[a]	1205	−91	−20			
E_2'	1312	1268[a]	−44	−6			
A_1'	1331	1270	−61	−33	8.1	18.0	5.6×10^{-6}
E_2'	1365	1328	−37	−24	9.6	13.9	2.3×10^{-6}
E_2'	1444	1377	−67	−50	11.8	20.8	4.3×10^{-6}
E_1''	1459[a]	1390[a]	−69	−66			
A_1'	1467	1404	−63	−45	11.8	19.4	3.5×10^{-6}
E_1''	1490[a]			−67			
E_2'	1512	1425	−87	−87	10.3	13.9	1.6×10^{-6}
E_2'	1565	1508	−57	−98	10.6	18.1	3.1×10^{-6}

[a] Weak peaks.

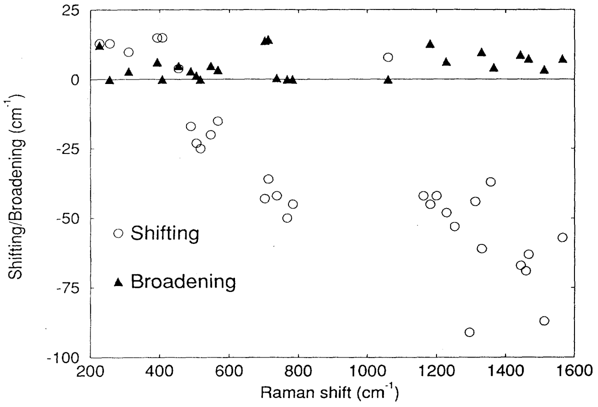

FIG. 2. The shifting and broadening of Raman modes of C_{70} upon K intercalation. Here the shifts are plotted as $\Delta\omega = \omega(K_4C_{70}) - \omega(C_{70})$ and the broadening is expressed by $\Delta\Gamma = \Gamma(K_4C_{70}) - \Gamma(C_{70})$ where Γ is the full width at half maximum intensity of a peak.

We identify the stoichiometry K_4C_{70} with the maximum conductivity σ on the basis of band-structure calculations,[8,16] according to which the lowest unoccupied molecular orbital (LUMO) for C_{70} is identified with the non-degenerate A_1'' level. A simplified picture suggests[10] that the first σ maximum observed in the doping process corresponds to the half-filling of the A_1''-derived band. The second σ maximum corresponds to the half-filling of the higher lying E_1'' band, which occurs when four electrons have been transferred per C_{70}. However, we did not carry out any characterization studies for the films to confirm the stoichiometry, nor did we confirm the level symmetry.

We first analyze the observed mode shifts in Fig. 1. In general, the high-frequency modes ($\omega > 500$ cm^{-1}) are down-shifted upon K intercalation, while those of low-frequency are up-shifted. The Raman-mode down-shifting has been observed in alkali-metal-doped C_{60} (Refs. 12 and 15) and in graphite intercalation compounds (GICs),[11] and is generally attributed to the C-C bond-length increase induced by charge transfer to the graphene layers from the donor intercalate.[11,12] We propose that the same charge transfer effects are also responsible for the down-shifting of C_{70} Raman modes.

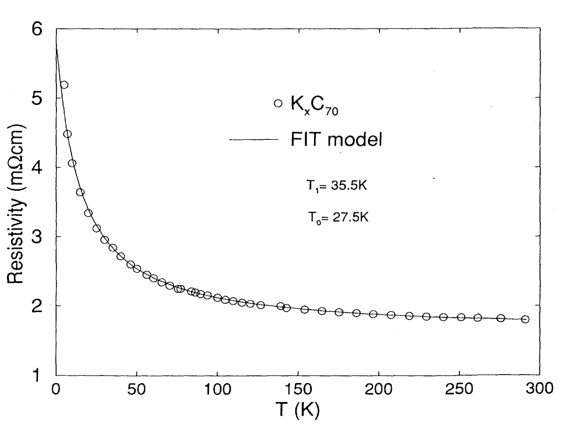

FIG. 3. The temperature dependence of the resistivity of a K_xC_{70} thin film at the maximum conductivity phase. The solid line is calculated according to the fluctuation-induced tunneling model for the idicated values of T_0 and T_1 (see text).

According to the model by Chan *et al.*[11] relating mode frequency shift in donor GICs to the charge transfer f_c per C atom $\Delta\omega = -880 f_c$ and using f_c=4/70=0.057 for K_4C_{70}, we obtain $\Delta\omega$=50 cm^{-1}, in agreement with the experimental values of 40–90 cm^{-1}, depending on the mode and its symmetry. Based on the same principle, Jishi and Dresselhaus have proposed a model[12] relating a force-constant change for C_{60} to a frequency shift and they obtained $\Delta K = -16.7 f_c$ eV/Å^2, where K is the force constant. The relation $\Delta\omega/\omega = \Delta K/2K$ leads to $\Delta\omega \sim$23 cm^{-1} for a mode nominally at ω=1500 cm^{-1}, on the same order as the observed value for C_{70} as well. A more sophisticated approach using a force-constant model has been applied to M_6C_{70} by Jishi *et al.*,[13,14] who predict a down-shift on the order of 20–90 cm^{-1} (see Table I), depending on the mode and its symmetry.

The up-shifting of low-frequency modes can be qualitatively explained by the Jishi-Dresselhaus mechanism.[12] This mechanism considers a change in electromagnetic force for a radial vibration of a charged carbon ball, which causes an increase in ω by

$$\Delta\omega^2 = \frac{3.4Qq}{R^3 m} \tag{1}$$

where Q is the total charge on the ball, q the average charge on each C atom, R (=3.7 Å for C_{60}) the radius of the ball, and m the mass of a C atom. Corrections associated with the ellipsoidal shape of the charged ball were not considered. The prefactor 3.4 arises from a nonuniform distribution of charges on the surface.[12] For K_4C_{70}, $\Delta\omega = 1400/\omega \sim 5.6$ cm^{-1} for $\omega \sim 250$ cm^{-1}, on the same order as the observed frequency up-shifting ($\sim$ 13 cm^{-1}). The force-constant model by Jishi *et al.* also predicts a similar up-shifting in M_6C_{70} (see Table I).[13,14]

Previous experiments on "saturated" M_xC_{70}[17] (M=K, Rb, and Cs) are qualitatively different from the results reported here. The Raman shifts reported there were on the average somewhat smaller than those in Table I, which seems to indicate a lower alkali-metal concentration. This discrepancy remains to be resolved. The experiments reported here were done on samples doped at a somewhat lower temperature.

We now turn to discuss the broadening of the Raman lines. The Raman-line broadening in K_4C_{70} is qualitatively different from that of K_3C_{60}.[6,7] In the K_4C_{70}, all the Raman lines are still relatively sharp and distinguishable so that every single mode found in the pristine C_{70} spectrum has its correspondence in K_4C_{70}. In contrast, in K_3C_{60} a few H_g lines are missing from the Raman spectrum due to the severe line broadening. There are many factors which might contribute to the broadening of a Raman line, such as inhomogeneity of doping, electron-phonon interaction, etc. For inhomogeneous broadening, we would expect a correlation between the line broadening and shifting, with larger shifts resulting in a broader linewidth. Figure 2, however, displays very little correlation between broadening and shifting, suggesting that inhomogeneity does not play a major role in line broadening.

Assuming that the electron-phonon interaction is the primary source for the line broadening, we can estimate an upper limit to the electron-phonon coupling constant λ in K_4C_{70} according to[18]

$$\lambda = \frac{2}{\pi g(0)} \sum_i \frac{\gamma_i}{\hbar\omega_i^2}, \tag{2}$$

where γ_i is the half width at half maximum intensity of a phonon mode with frequency ω_i, $g(0)$ is the electronic density of states at the Fermi level per spin per C_{70}, and the sum is over all the optical branches i at wave vector q=0. To obtain Eq. (2), we ignore the dispersion of the optical branches. Since inhomogeneity may contribute to part of the line broadening, Eq. (2) is an overestimate which sets an upper limit of λ. According to the argument advanced by Varma *et al.*[2] for K_3C_{60}, only those Raman-active phonon modes in K_4C_{70}, with A_1' and E_2', symmetry are relevant with regard to superconductivity, since the electronic states of K_4C_{70} at the Fermi level have E_1'' symmetry.[16] According to this argument, two electrons each with symmetry E_1'' are coupled by a phonon with symmetry constrained by the direct product

$$E_1'' \otimes E_1'' = A_1' + A_2' + E_2' \tag{3}$$

which contains the Raman active A_1' and E_2' modes, while A_2' corresponds to the antisymmetric component of the Raman tensor which does not give rise to Raman-active modes.

Adding up the contributions (the contributions to λ from the missing allowed modes in the Raman spectra are included by assuming that each of them exhibits an average broadening) (see Table I) from the Raman-active A_1' and E_2' modes as was done for K_3C_{60},[2,3,6,7] we obtain $\lambda g(0) = 1.5$ (eV spin $C_{70})^{-1}$ after correcting for the different slit widths used for measuring C_{70} and K_4C_{70}. The density of states factor $g(0)$ can be obtained from the thermopower data[9] which imply a Fermi energy of E_F=0.25 eV. Thus

$$g(0) = \frac{3n}{2E_F} = 12 \text{ states/(eV spin } C_{70}), \tag{4}$$

where n is the number of free electrons per C_{70}. (We take n=2 for the half-filled E_1'' conduction band which can accommodate a total of four electrons.[8–10]) We thus obtain an upper-limit estimate of λ=0.1. Since this value lies within the range of the Coulomb repulsion[2,3] μ^*=0.1–0.2, a superconducting state is unlikely to be formed by the intramolecular electron-phonon interaction. We argue that the much larger value of $\lambda g(0)$ obtained for K_3C_{60} by observation of the line broadening of the intramolecular Raman-active modes[7] suggest that the intramolecular electron-phonon interaction mechanism is primarily responsible for superconductivity in K_3C_{60}.

In conclusion, we investigated the Raman spectrum of K_xC_{70} for the maximum-conductivity phase (nominally x=4). The frequency shift upon K intercalation can be understood by a bond-length change induced by charge transfer and a mode stiffening induced by an electromagnetic force. Assuming that the intramolecular electron-phonon interaction is a major source for doping-induced line broadening, we find that the magnitude of λ lies within the range of μ^*, thereby explaining the absence of superconductivity of K_xC_{70} through the intramolecular electron-phonon interaction.

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