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Raman study of the two-dimensional polymers Na_4C_{60} and tetragonal C_{60}

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We present a Raman investigation of the monoclinic two-dimensionally polymerized phase Na_4C_{60} and a comparison with the pure tetragonal C_{60} polymer and the doped K_3C_{60} structure. The Raman spectrum of Na_4C_{60} depends on the probing laser wavelength, and high wave-number modes are hard to observe with a low-energy laser excitation. The spectrum for Na_4C_{60} is very rich with a pronounced splitting of the original H_g modes and a large number of new modes. Several modes at low wave numbers support the presence of intermolecular bonds and the line broadening observed for low-frequency H_g modes is typical for electron-phonon coupling in metallic fullerene systems. From the shift of the pentagonal pinch mode we deduce an unexpectedly low charge transfer of approximately three electrons per C_{60} molecule. The presence of a distinct mode around 980 cm^{-1} throws doubts on earlier assumptions that modes in this range are connected to vibrations in the intermolecular cyclobutane rings found in C_{60} polymers. No superconductivity is observed in Na_4C_{60}, although the electron-phonon interaction derived from the Raman spectrum is similar to that in K_3C_{60}.

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INTRODUCTION

After the discovery of a new class of carbon materials, the fullerenes, by Kroto *et al.*[1] in 1985, carbon research has evolved in several new directions because of the many interesting properties of the most stable fullerene, C_{60}. As one example, on intercalation with alkali metals C_{60} often transforms into a metallic, superconducting state, with a critical temperature as high as 40 K for Cs_3C_{60}.[2] Even without chemical doping, C_{60} can be transformed into a superconductor by field-effect doping in a field-effect transistor (FET) geometry,[3] and by additionally expanding the lattice through chemical doping an extremely high transition temperature of 117 K has recently been reached.[4] Another interesting fact is that C_{60} can easily be transformed from the original cubic van der Waals bonded structure into one-, two-, and even three-dimensionally connected polymers.[5–7] In the quasi-two-dimensional rhombohedral polymeric phase, weak ferromagnetism with a Curie temperature near 500 K has recently been observed.[8]

Since doped and polymeric fullerenes show such interesting properties, it is obviously of interest to investigate fullerene materials which are *both* doped and polymerized. The only well characterized quasi-two-dimensional doped fullerene polymer is Na_4C_{60}, which is reported to have a body-centered monoclinic structure with space group $I2/m$ at temperatures below 550 K.[9,10] While pure C_{60} usually polymerizes by a $[2+2]$-cycloaddition reaction, which creates two C-C bonds, forming a four-atom cyclobutane carbon ring, between each pair of molecules, Na_4C_{60} has been reported to have single C-C bonds between molecules. Such single-bonded structures have also been reported for some alkali-metal doped linear-chain polymers, such as Na_2RbC_{60},[11] and for AC_{60} dimers.[12] Sodium intercalated C_{60} compounds behave in many ways different from compounds containing heavier alkali metals because of the small size of the Na ions. For example, while most A_4C_{60} compounds are nonmetallic, Na_4C_{60} is believed to be a strongly correlated metal.[9] Also, samples with a nominal composition Na_4C_{60} but possibly containing an unknown amount of nitrogen or other impurities have been reported to be superconducting with transition temperatures up to 15 K.[13]

Many properties of Na_4C_{60}, including details of the phonon spectrum[14,15] have already been studied in detail. However, although several Raman spectra have been presented,[10,14,15] they have never been discussed in detail. Since Raman spectroscopy is a very powerful tool to characterize other polymeric and/or doped phases of C_{60}, a large amount of information can potentially be obtained by comparing the Raman spectrum of Na_4C_{60} with those of other doped or polymerized phases of C_{60}. Of particular interest is then the two-dimensionally polymerized tetragonal phase of C_{60}. Each C_{60} molecule in this phase is covalently bonded to four neighbors, as in Na_4C_{60}, but the tetragonal phase has the cycloadduct type of intermolecular bonds.[7,16,17] We have recently studied the structure and Raman spectrum of the tetragonal phase in detail,[17,18] using both polycrystalline and single-crystal C_{60} as starting materials for the polymerization reaction. Our studies showed that this phase has a $P4_2/mmc$ symmetry with successive polymer layers rotated by 90° about the stacking axis.[17]

We have now measured the Raman spectrum of Na_4C_{60} using three different excitation lasers and compared the resulting spectra with those for tetragonal (polymeric) C_{60} and (doped, metallic) K_3C_{60}. The Raman spectrum of Na_4C_{60} shows many interesting features. Some of them are typical for fullerene polymers while others can be traced to doping effects. One particularly interesting feature is the appearance of a strong Raman band just below 1000 cm^{-1}. Features in this frequency range are usually attributed to vibrations in the intermolecular cyclobutane rings in polymeric phases of pure C_{60}, but with the assumed structure of Na_4C_{60} no such feature would be expected. The H_g modes in Na_4C_{60} also show a strong broadening which might arise from electron-phonon interactions. In view of the possible observation of

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superconductivity in a closely related material[13] we have tried to derive the strength of the electron-phonon coupling from the Raman data, a method previously applied to both metallic and nonmetallic fullerene compounds.

EXPERIMENTAL METHODS

The pressure polymerized tetragonal sample was produced by treating polycrystalline C_{60} powder[19] at 2.5 GPa and 830 K for six hours in a piston-cylinder device with a Teflon pressure cell containing a helical internal heater. To maximize phase purity we used a pressure-temperature trajectory similar to that used by Moret *et al.*[17] The sample was encased in a thin-walled stainless-steel cylinder inserted into the heater. As pressure medium we used a mixture of talc and glass beads. The talc has been shown to give a quasihydrostatic pressure and the glass beads are used as thermal insulation at the walls of the Teflon cell.[20] The pressure polymerized sample was handled in air but stored in an evacuated chamber between measurements.

The Na_4C_{60} and K_3C_{60} samples were produced by mixing stochiometric amounts of C_{60} and alkali metals under Ar gas in a glove box with oxygen and water levels below 1 ppm. The samples were then placed in glass tubes and heated for two weeks at 630 and 520 K for the Na_4C_{60} and K_3C_{60} sample, respectively. During this period the samples were ground twice, to increase the homogeneity. After the heat treatment the temperature was slowly decreased to room temperature and the samples were sealed in Lindemann capillaries without any exposure to ambient atmosphere.

The Raman studies were performed using a Renishaw 1000 grating spectrometer with a notch filter to remove the Rayleigh line and a Peltier cooled charge-coupled device (CCD) detector. As probing lasers we used three different wavelengths, an argon-ion laser (514.5 nm), a He-Ne laser (632.5 nm), and a diode laser (782 nm). The power densities of the lasers on the sample were smaller than 10 W/cm^2. The low power density was used to ensure that no additional photoinduced polymerization occurred in the samples and to avoid sample heating. The resolution of the Raman spectra was about 2 cm^{-1}. The x-ray powder-diffraction experiment was carried out using the Cu K_α line and a Philips powder-diffraction system with a PW1820 goniometer. We also measured the magnetic susceptibility of our sample using a MagLab System 2000 from Oxford Instruments.

RESULTS AND DISCUSSION

The x-ray data on Na_4C_{60} (not shown here) were in excellent agreement with literature data on this phase.[9] We thus assume that the material has a body-centered monoclinic structure with space group $I2/m$ and single C-C intermolecular bonds, as reported in the literature.

One sample was annealed under high pressure and temperature, near 2.5 GPa and 800 K, for 5 h to see if this treatment would change the structure or other properties. However, as reported elsewhere,[21] this treatment only sharpened the original x-ray diffraction and Raman lines, indicating that the structural purity was improved. Na_4C_{60} is thus very stable under high-pressure conditions, not only at low temperature[10] but also well above room temperature.

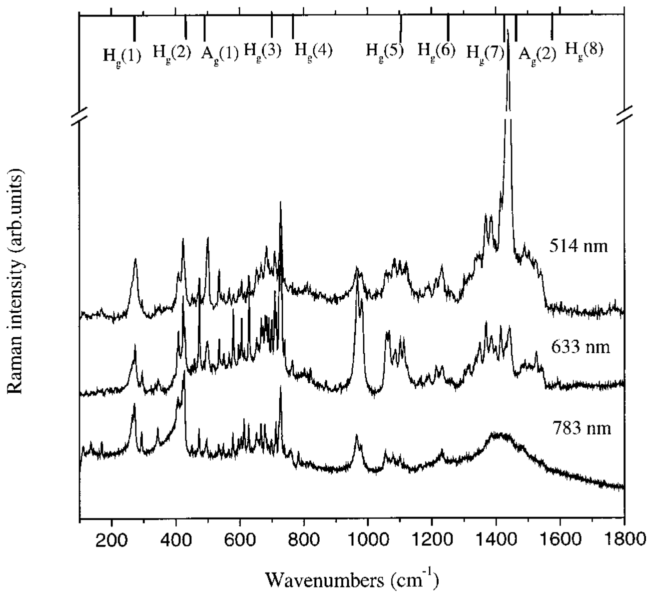

FIG. 1. Raman spectra for Na_4C_{60}, after elimination of backgrounds, excited with the wavelengths shown. Thick lines at the top show the positions of the ten Raman active modes in pristine C_{60}.

As mentioned above, the vibrational spectra of both monomeric and polymeric Na_4C_{60} have already been studied by inelastic neutron scattering.[14] Neutron scattering is not limited by selection rules and because of the very large number of degrees of freedom in both pristine, doped, and polymerized C_{60} it is difficult to obtain detailed information on individual modes by this method. However, the low-frequency acoustic and librational modes are very strongly modified by polymerization, as might be expected. Below 25 meV the generalized density of states for the quasi-two-dimensional polymer Na_4C_{60} differs greatly from those for pristine C_{60}, linear-chain C_{60} compounds, or the monomeric high-temperature form of Na_4C_{60}. On the other hand, a comparison with inelastic neutron-scattering data for the tetragonal phase of C_{60} (Refs. 15 and 22) shows large similarities in the energy dependence as might be expected for two topologically similar phases. However, the phonons of Na_4C_{60} are "softer," with a maximum in the density of states near 14 meV (versus 20 meV for the tetragonal phase), probably because of the smaller number of intermolecular bonds.

Raman spectroscopy, on the other hand, is governed by strict selection rules. The free isolated C_{60} molecule exhibits ten (two A_g + eight H_g) Raman allowed modes. At room temperature the crystal-field effects due to the T_{6h} space group are very small and therefore the room-temperature Raman spectrum of C_{60} also contains the same ten modes. The positions of these are shown as thick vertical lines at the top of Fig. 1, which shows Raman spectra of Na_4C_{60} obtained using the three different excitation wavelengths given above. When the highly symmetric pristine C_{60} material is doped to the monoclinic Na_4C_{60} structure with space group $I2/m$ and single polymer bonds, the symmetry is lowered significantly. This leads to a splitting of the fivefold degenerate H_g modes and the appearance of many modes that were optically silent earlier. In addition to this, vibrational modes, characteristic for the new structure, are created. Examples of these are the intermolecular modes at low wave numbers seen at 113, 137, and 169 cm^{-1} and the wide band between 950 and 1000 cm^{-1}.

Leaving the discussion of individual modes until later, we begin by observing that there are large differences between Raman spectra obtained for different probing laser wavelengths. It is known from several earlier studies that the Raman response of many fullerene based materials depends strongly on the probing wavelength. Nanotubes, which can be seen as elongated fullerenes, exhibit a strong resonance in the "red" frequency range due to van Hove singularities in their densities of states,[23] and for doped metallic fullerenes strong enhancements may occur depending on both the strength of the electron-phonon coupling and the probing laser wavelength.[24] For some polymeric phases of pure C_{60} the vibrational modes are difficult to observe when excited with low-energy lasers due to a very high background probably coming from broadband luminescence.[25,26] Still, although the spectra in Fig. 1 are visually very different, closer scrutiny shows that they are really very similar except at "high" wave numbers, above about 1200 cm^{-1}. All vibrations are found at the same positions for different excitation wavelengths and only the intensities of the modes vary. Some differences should, however, be noted. At low wave numbers, the intermolecular modes are much easier to observe for the diode laser, and for the same laser the low-frequency H_g modes, especially the $H_g(2)$ mode, show a slightly stronger broadening. However, larger differences between the spectra are seen at wave numbers over 1200 cm^{-1}. For the diode laser the upper H_g modes and the $A_g(2)$ mode are completely smeared out, making it impossible to identify individual vibrational modes. The spectra obtained with the He-Ne laser and the argon-ion laser are more similar and all components of the split $H_g(7)$ and the $H_g(8)$ modes can be seen in both spectra. A very striking detail is that the pentagonal pinch mode at 1441 cm^{-1} is invisible with the diode laser, almost absent for the He-Ne laser excitation but the strongest mode when excited with the argon-ion laser.

To enable a comparison between pristine and tetragonal C_{60}, Na_4C_{60}, and doped K_3C_{60}, we show in Fig. 2 the Raman spectra of the last three of these, again with the ten lines of pristine C_{60} shown at the top of the figure. As a first general comment, we note that doping in itself (K_3C_{60}) does not necessarily change the symmetry significantly and does not increase the number of lines very much. Conversion to the tetragonal structure, with covalent cyclobutane-type intermolecular bonds between each molecule and its four nearest neighbors, significantly increases the number of Raman lines, and doping to the Na_4C_{60} structure, with its even lower monoclinic symmetry, gives a further increase. This is particularly obvious in the range 500–700 cm^{-1}. Most of these "new" lines are existing modes which were previously optically silent or forbidden in the original I_h symmetry, but some are also connected with the formation of the polymerized structure and the introduction of the dopant ions.

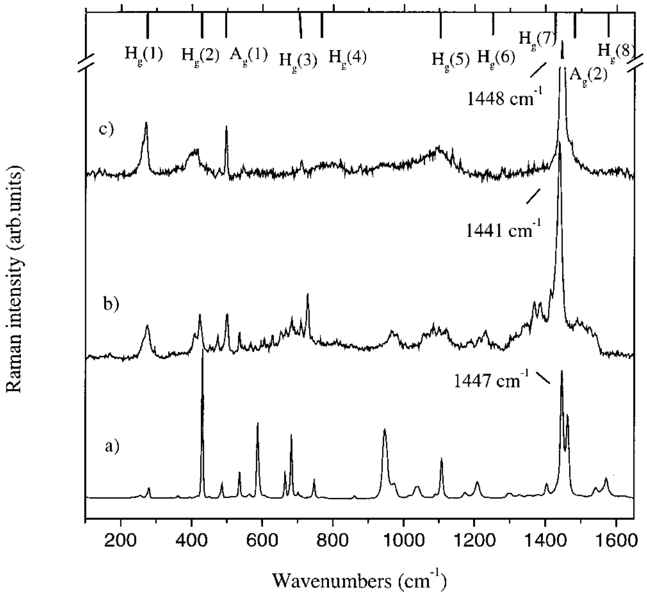

FIG. 2. Raman spectra excited with an argon-ion laser (514.5 nm) for (a) pure tetragonal C_{60}, (b) Na_4C_{60}, and (c) K_3C_{60}. Thick lines at the top show the positions of the ten Raman active modes in pristine C_{60}.

To facilitate the comparison of individual modes we have listed the observed Raman frequencies and their probable assignment for Na_4C_{60} and tetragonal C_{60} in Table I. A similar list for several pressure polymerized C_{60} phases has been presented by Davydov *et al.*[25] Starting in the range below the lowest $H_g(1)$ mode of pristine C_{60}, we find new modes at 113, 137, and 169 cm^{-1} for Na_4C_{60} and at 153 and 171 cm^{-1} for tetragonal C_{60}. Such low-frequency intermolecular Raman modes are also found in the linear C_{60} polymers[27] and can be assigned to stretching and bending modes in the polymer network. A particularly interesting set of new modes in the spectra can be seen at 946 and 974 cm^{-1}, and 966 and 980 cm^{-1} for the tetragonal and Na_4C_{60} phases, respectively. Such modes are observed in all polymers connected by four-membered carbon rings, although at slightly different positions. Since the carbon ring stretch mode for cyclobutane is also found around 1000 cm^{-1},[28] this mode has long been assigned to vibrations in the four-carbon ring itself. Calculations of the Raman spectrum of polymeric C_{60} also show that a mode at 967 cm^{-1} is to 85% connected to the displacement of the four atoms participating in the four-carbon ring.[29] It is therefore very surprising to find a mode at virtually the same position for the presumably *single*-bonded Na_4C_{60} polymer. However, earlier studies by Renker *et al.*[14,15] show similar features. For other single-bonded polymers studied with Raman spectroscopy, such as the quenched RbC_{60} dimer phase,[30] no such mode has been reported and we find no Raman data in the literature for the single-bonded linear polymers. There are two possible interpretations for the appearance of these modes in Na_4C_{60}: either the modes do not represent ring stretch vibrations in a four-carbon ring, but some other vibration associated with all sp^3-type intermolecular bonds, or the assumed structure with single C-C bonds between the molecules is not correct. The single-bonded polymer structure has strong support from both x-ray

TABLE I. Observed Raman mode frequencies and their assignment for Na_4C_{60} and tetragonal C_{60}.

Na_4C_{60}	Tetragonal C_{60}	Assignment Na_4C_{60}T C_{60}	Na_4C_{60}	Tetragonal C_{60}	Assignment Na_4C_{60}T C_{60}
113 cm^{-1} (w)		intermolecular ν stretch mode	698 cm^{-1} (w)	701 (w)	$H_g(3)$ parent mode
137 cm^{-1} (w)	153 (w)	intermol. mode δ_x bend. mode	708 cm^{-1} (m)	709 (w)	$H_g(3)$ parent mode
169 cm^{-1} (w)	171 (w)	intermol. mode δ_y bend. mode	715 cm^{-1} (m)		$H_g(3)$ parent mode
265 cm^{-1} (m)	255 (w)	$H_g(1)$ parent mode	724 cm^{-1} (s)		$H_g(3)$ parent mode
273 cm^{-1} (s)	280 (m)	$H_g(1)$ parent mode	728 cm^{-1} (s)		$H_g(3)$ parent mode
294 cm^{-1} (m)	361 (w)	$H_g(1)/F_{2u}(1)$ parent mode	741 cm^{-1} (m)	748 (m)	$H_g(4)$ parent mode
406 cm^{-1} (m)		$H_g(2)$ parent mode	765 cm^{-1} (w)	771 (w)	$H_g(4)$ parent mode
421 cm^{-1} (s)	415 (w)	$H_g(2)$ parent mode	784 cm^{-1} (w)	862 (w)	$H_g(4)/F_{2g}(2)$ parent mode
428 cm^{-1} (m)	430 (s)	$H_g(2)$ parent mode	966 cm^{-1} (m)	946 (s)	bridge bond
451 cm^{-1} (w)	450 (m)	$H_g(2)$ parent mode	980 cm^{-1} (m)	974 (m)	bridge bond
459 cm^{-1} (w)		$H_g(2)$ parent mode	1059 cm^{-1} (m)	1015 (w)	$H_g(5)/F_{2u(3)}$ parent mode
473 cm^{-1} (m)	485 (m)	$H_g(2)/A_g(1)$ parent mode	1066 cm^{-1} (m)	1038 (m)	$H_g(5)/F_{2u}(3)$ parent mode
500 cm^{-1} (s)		$A_g(1)$ parent mode	1084 cm^{-1} (m)	1090 (w)	$H_g(5)$ parent mode
513 cm^{-1} (w)	512 (w)	$F_{1g}(1)$ parent mode	1101 cm^{-1} (m)		$H_g(5)$ parent mode
535 cm^{-1} (m)	534 (m)	$F_{2g}(1)$ parent mode	1112 cm^{-1} (m)	1108 (m)	$H_g(5)$ parent mode
542 cm^{-1} (w)		$F_{1u}(1)$ parent mode	1193 cm^{-1} (w)	1174 (w)	$H_g(6)$ parent mode
549 cm^{-1} (w)		$F_{1u}(1)$ parent mode	1215 cm^{-1} (w)	1208 (m)	$H_g(6)$ parent mode
565 cm^{-1} (w)	563 (w)	$F_{2g}(1)$ parent mode	1232 cm^{-1} (m)		$H_g(6)$ parent mode
579 cm^{-1} (w)	585 (s)	$F_{1u}(2)/F_{2g}(1)$ parent mode	1302 cm^{-1} (w)	1301 (w)	$G_u(5)$ parent mode
596 cm^{-1} (w)		$F_{1u}(2)$ parent mode	1343 cm^{-1} (w)	1327 (w)	$G_g(5)/G_{1g}(3)$ parent mode
605 cm^{-1} (w)		$F_{1u}(2)$ parent mode	1369 cm^{-1} (m)	1352 (w)	$G_g(5)/F_{1g}(3)$ parent mode
615 cm^{-1} (w)		$G_g(2)$ parent mode	1386 cm^{-1} (m)	1378 (w)	$H_g(7)$ parent mode
629 cm^{-1} (w)		$G_g(2)$ parent mode	1416 cm^{-1} (m)	1432 (s)	$H_g(7)$ parent mode
638 cm^{-1} (w)		$G_g(2)$ parent mode	1440 cm^{-1} (s)	1447 (s)	$Ag(2)$ parent mode
653 cm^{-1} (m)		$G_g(2)$ parent mode		1464 (s)	dimer phase
667 cm^{-1} (m)	665 (m)	$H_g(3)$ parent mode	1489 cm^{-1} (w)	1541 (s)	$H_g(8)$ parent mode
683 cm^{-1} (m)	683 (s)	$H_g(3)$ parent mode	1525 cm^{-1} (w)	1564 (w)	$H_g(8)$ parent mode
689 cm^{-1} (m)		$F_{2u}(2)$ parent mode	1543 cm^{-1} (w)	1572 (m)	$H_g(8)$ parent mode

diffraction[9] and differential scanning calorimetry experiments,[31] as well as from both inelastic neutron-scattering measurements and theoretical calculations.[14] The first explanation should therefore be more likely.

In pristine C_{60} the most frequently studied Raman mode is the $A_g(2)$ pentagonal pinch mode at 1469 cm^{-1}. This mode shows a strong shift to lower wave numbers when C_{60} is doped with alkali metals or when it is polymerized to different structures. The shift has been shown to depend linearly on the charge transferred from alkali atoms to the C_{60} molecule, with a downshift of ~ -6 cm^{-1}/electron charge.[32] The shift has also been shown to depend almost linearly on the number of intermolecular bonds per molecule, such that the mode shifts ~ -5.5 cm^{-1}/intermolecular bond.[25,33] Our results are in excellent agreement with this empirical model for the tetragonal polymer [Fig. 2(a)], with four polymer bonds per molecule, and the unpolymerized K_3C_{60} phase [Fig. 2(c)], with a charge transfer of three electrons per molecule. Using this model for the Na_4C_{60} phase is somewhat more questionable. For the linear doped polymers RbC_{60} and KC_{60}, it has been shown that the two shifts are additive.[34] If one takes into account that the Na_4C_{60} polymer has four single intermolecular bonds/molecule, a shift of the pentagonal pinch mode to 1441 cm^{-1} indicates a charge transfer of approximately three electrons per C_{60} molecule. This is a surprisingly small value, considering that alkali-metal intercalation usually leads to a full charge transfer. Kubozono *et al.*[10] find a shift to 1438 cm^{-1} and calculate a charge transfer of a full four electrons per molecule, taking no account to the effects of intermolecular bonds. However, since all previous studies show that the formation of such bonds is reflected in a mode shift, our feeling is that such effects must be taken into account. Armbruster *et al.*[35] have studied the electronic structure of very thin films of $\mathrm{Na}_x\mathrm{C}_{60}$. For a sample with nominal composition $x=4$, but an unspecified structure, they find full charge transfer, but for heavily doped samples $(x>8)$ the charge transfer is incomplete. An incomplete charge transfer has also been observed for $\mathrm{Li}_x\mathrm{CsC}_{60}$ compounds.[36] It thus seems that the light alkali metals Li and Na do not conform to the common assumption that alkali-metal doping of fullerenes leads to a complete charge transfer.

From Fig. 2 it is also clear that the splitting of the H_g modes is much more pronounced for $\mathrm{Na}_4\mathrm{C}_{60}$ than for tetragonal C_{60}, probably because of the low symmetry and interactions between sodium atoms and fullerene molecules. The low-frequency H_g modes of $\mathrm{Na}_4\mathrm{C}_{60}$ are especially broad, resembling those of metallic $\mathrm{K}_3\mathrm{C}_{60}$ and very different from the sharp modes seen for the tetragonal phase. For both materials this broadening is assigned to electron-phonon coupling between the phonons on the C_{60} molecules and the band electrons derived from alkali-metal ions. It might be expected that the low-frequency H_g modes should be more broadened than the high-frequency modes since the former have a more radial character.

Because superconductivity has been reported in a phase[13] closely related to $\mathrm{Na}_4\mathrm{C}_{60}$ it is of some interest to analyze the electron-phonon coupling strength in $\mathrm{Na}_4\mathrm{C}_{60}$ to see whether it is sufficient to explain such an effect. If so, $\mathrm{Na}_4\mathrm{C}_{60}$ might be the first doped polymeric fullerene superconductor.

The broadening of phonon modes in the Raman spectrum, as measured as the full width at half maximum (FWHM), comes from several different processes. For nonmetallic systems, the measured linewidth can be increased by instrumental broadening, phonon-phonon interactions, and phonon scattering by lattice disorder. For systems with free carriers another process, called Landau damping, may contribute to the phonon linewidth. It occurs if Δk, the wave-vector transfer between the photons and optic phonons, is sufficiently large to cause intraband electron scattering.[37] For ordered systems this requires moderate Fermi velocities and large Δk, which basically means that low-frequency modes together with a high energy of the probing laser have a larger chance to be candidates for Landau damping, but if sufficient disorder exists this can also occur without any constraint on Δk.[37] The relation between phonon linewidth and electron-phonon coupling constants for a single-particle excitation, Allen's formula, may be used in the form[38]

$$\gamma_i=\frac{2\pi}{g_i}N(0)\lambda_i\omega_{bi}^2, \tag{1}$$

where γ is the FWHM of a specific mode, g_i is the mode degeneracy (5 for H_g modes), $N(0)$ is the density of states per spin and molecule at the Fermi level, and λ is the dimensionless electron-phonon coupling constant. For ω one should use the bare phonon frequency for the vibration before any coupling to the electrons. For doped unpolymerized systems, the phonon frequency in pristine C_{60} is normally used as the bare frequency. In our system this procedure is complicated by the fact that the modes might be influenced by the intermolecular bonds. However, at least for tetragonal C_{60} the shift and splitting of the low-frequency H_g modes are small, and since the overall electron-phonon coupling constant is almost completely dominated by the first two H_g modes, it should be possible to use the frequencies for pristine C_{60} as bare frequencies without introducing a large error.

For alkali-metal intercalated fullerene compounds it is not obvious that Allen's formula is applicable. However, the broadening of the H_g modes was one of the most important indications that the BCS model could be applied to fulleride systems,[39–41] and the Raman method has been used to find λ in many fullerene materials. Zhou *et al.*[42] obtained values for λ of 0.6 and 0.5 for $\mathrm{K}_3\mathrm{C}_{60}$ and $\mathrm{Rb}_3\mathrm{C}_{60}$, respectively, resulting in realistic values for the transition temperatures, while Wang *et al.*[43] found a value of 0.1 for $\mathrm{K}_4\mathrm{C}_{70}$, explaining why the latter is not a superconductor in contrast to the two C_{60} compounds. Later, similar analyses have been carried out by Winter *et al.*[24,34] on $\mathrm{K}_3\mathrm{C}_{60}$ and RbC_{60}.

To find the total electron-phonon interaction constant λ we need to know $N(0)$. Following Winter and Kuzmany,[24] we have tried to calculate an approximate value for $N(0)$ using a linear relation between the Raman shift, and the linewidth γ,

$$\gamma=-\frac{\pi}{2}N(0)\omega_b\Delta\omega, \tag{2}$$

where $\Delta\omega$ is the difference between the bare phonon frequency for pristine C_{60} and the observed position in $\mathrm{Na}_4\mathrm{C}_{60}$. For $\mathrm{K}_3\mathrm{C}_{60}$ there is a striking difference between the appearances of the $H_g(1)$ and $H_g(2)$ modes and those of higher modes, for which there is no relation between shift and line broadening.[24] We have assumed that we can use relation (2) for at least the lowest frequency mode $H_g(1)$. A peak-fitting program has been used to resolve the five components of the originally fivefold degenerate $H_g(1)$ mode and the phonon linewidth (FWHM) has been plotted against the observed line shift in Fig. 3, using the bare phonon frequency $\omega_b=270\ \mathrm{cm}^{-1}=0.034$ eV. The electron density of states is proportional to the slope of the resulting line in Fig. 3 and we deduce values of $N(0)=4.5$, 7.2, and 8.4 eV^{-1} for the diode, the He-Ne, and the argon-ion laser, respectively. The discrepancies between the results for different lasers might mean that Allen's theory is not applicable to our system. However, it might also arise from other effects, such as different sample heating for different lasers, or from the error introduced when using the bare phonon frequency of pristine C_{60}, since we do not know the Raman spectrum for an undoped *single bonded* two-dimensional polymer system. The average value for $N(0)$, 6.7 eV^{-1}, is reasonable if we compare with the value 12 eV^{-1} reported for $\mathrm{K}_3\mathrm{C}_{60}$ obtained with the same method,[24] since the smaller intermolecular distance in the polymer should lead to a broadening of the bands. On the other hand, Kubozono *et al.*[10] deduced a much smaller value

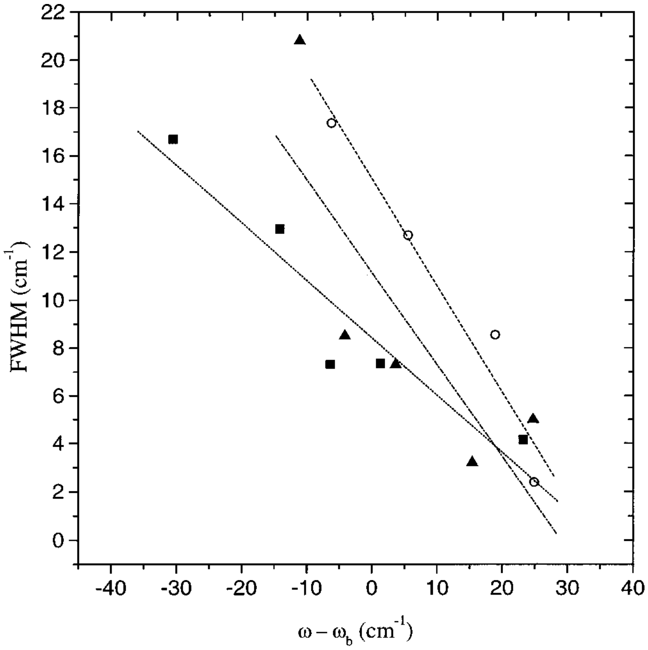

FIG. 3. Plot of linewidth (FWHM) versus observed frequency shift, ω-ω_b, for the components of the $H_g(1)$ mode. Squares show results for the diode laser (782 nm), triangles for the He-Ne laser (632 nm), and circles show the results for the argon-ion laser (514 nm).

of 2 eV^{-1} from electron spin resonance (ESR) studies. However, different methods very often give widely different values for $N(0)$ in doped fullerenes.[40,42]

The value $N(0)=6.7\ \mathrm{eV}^{-1}$ can now be used together with Eq. (1) to calculate both the total overall electron-phonon interaction factor λ and the contributions from the individual H_g modes, with the results shown in Table II. For Na_4C_{60} we find a surprisingly large value $\lambda=0.3$. This value is similar in magnitude to the values for λ in K_3C_{60} given by Zhou *et al.*[42] ($\lambda=0.6$) and by Winter and Kuzmany[24] ($\lambda=0.25$), and to data for Rb_3C_{60} given by Zhou *et al.*[42] ($\lambda=0.5$). (The data from Winter and Kuzmany are corrected from the original paper[34] by a factor of 4.) For Na_4C_{60}, K_3C_{60}, and Rb_3C_{60}[24,42] experiments indicate that the main contributions to λ come from the low-frequency H_g modes, while theoretical calculations often show strong contributions also from higher modes.[39,40] However, while a dominant contribution to λ from $H_g(1)$ is found here and by Winter and Kuzmany, Zhou *et al.* find that the $H_g(2)$ mode dominates. We note also that although the highest and lowest frequency modes show larger line broadening than the intermediate frequency modes, the difference is not as large for Na_4C_{60} as that observed by Winter and Kuzmany for K_3C_{60}.

TABLE II. Mode positions, linewidths (FWHM), and electron-phonon coupling constants for the eight fivefold degenerate H_g modes. The values for the linewidths are given for the argon-ion laser (514 nm). The values for K_3C_{60} are corrected from the original paper (Ref. 34) by a factor 4.

			λ	
Mode	ω_b (cm^{-1})	γ (cm^{-1})	This work Na_4C_{60}	K_3C_{60} (Ref. 24)
$H_g(1)$	270	14	0.18	0.15
$H_g(2)$	430	10	0.052	0.06
$H_g(3)$	709	7	0.013	0.006
$H_g(4)$	773	9	0.014	0.009
$H_g(5)$	1101	15	0.012	0.003
$H_g(6)$	1248	14	0.009	0.003
$H_g(7)$	1426	12	0.006	0.013
$H_g(8)$	1573	15	0.006	0.009
Σ			0.296	0.25

We were surprised to find a total λ for Na_4C_{60} which is similar in magnitude to those of K_3C_{60} and Rb_3C_{60} and significantly larger than that of RbC_{60}.[34] While RbC_{60} is a nonsuperconducting phase, both K_3C_{60} and Rb_3C_{60} are well known to be superconducting at quite high temperatures. To test our sample for superconductivity we carried out a measurement of the magnetic susceptibility from room temperature down to 2 K. These measurements showed no significant diamagnetic signals, ruling out superconductivity in our material. Still, the measured value of λ is high enough that recent reports on superconductivity in a closely related material[13] cannot be ruled out. Our value for λ is, in fact, higher than the value 0.25 found for K_3C_{60} by Winter and Kuzmany.[24] The latter measurement was carried out at 80 K, while our study was carried out at room temperature. This might lead to a slightly larger broadening of our modes but we estimate that this temperature effect should only account for at most 10% of our total observed electron-phonon coupling constant. Another possible reason for the high value is that the value used for the density of states is too low. The total λ is proportional to $1/N(0)$, and a low value for $N(0)$ would give a high value for λ. We have tried to estimate $N(0)$ from experiments because the density of states in polymeric Na_4C_{60} is difficult to estimate theoretically. $N(0)$ depends on the charge transfer, and the band structure of C_{60} is modified by the presence of intermolecular bonds. Using instead $N(0)=12–15\ \mathrm{eV}^{-1}$, as for the A_3C_{60} compounds,[24,42] would reduce the value for the electron-phonon interaction parameter to $\lambda=0.13–0.16$ which is similar to that of K_4C_{70},[43] and low enough to explain the absence of superconductivity in our sample. However, such low values for λ are probably not realistic because the significantly smaller lattice parameter of Na_4C_{60} as compared to the A_3C_{60} compounds should lead to a smaller density of states.

To summarize, we have presented a detailed Raman investigation of polymeric Na_4C_{60}. The vibrational Raman spectra depend on the probing laser wavelength, making it hard to observe high wave-number modes with low-energy laser excitation. The Raman spectrum for Na_4C_{60} is very rich, with a pronounced splitting of the H_g parent modes and a large number of new modes. A number of modes at low wave numbers supports the presence of intercage bonds in the structure and the characteristic line broadening for low H_g modes is typical for metallic fullerene systems. From the shift of the pentagonal pinch mode we deduce that the charge transfer is no larger than three electrons per C_{60} molecule, if we take intermolecular bonds into account. The presence of a distinct mode around 980 cm^{-1} throws doubt on earlier assumptions that this mode is connected to the vibration in the four-member carbon rings found in double bonded polymers. The line broadening of the H_g modes indicate a fairly low density of states and an electron-phonon coupling constant λ which is comparable to that in K_3C_{60}. However, no superconductivity was observed down to 2 K in Na_4C_{60}.

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