Infrared and differential-scanning-calorimetry study of the room-temperature cubic phase of RbC$_{60}$

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We present differential-scanning-calorimetry curves and infrared spectra taken during the temperature cycling of stoichiometrically pure RbC$_{60}$ powder. In addition to the three known phases (high-temperature fcc, ortho-I, and ortho-II), we see evidence for an intermediate structure around 300 K, observed previously by ESR and x-ray diffraction. This phase is obtained both by quenching from high temperature and by warming up the ortho-II structure. Its infrared spectrum is identical to that of the high-temperature fcc phase, indicating a structure containing C$_{60}^-$ monomers.

Alkali salts of C$_{60}$ with 1:1 composition, KC$_{60}$ and RbC$_{60}$, have been the subject of intensive study, since their discovery two years ago.[1-3] These materials occur in several structural phases, which depend on their thermal history.[4] At room temperature, the stable phase is orthorhombic (called ortho-I), for which a structure containing one-dimensional polymer chains has been proposed.[5-7] The high-temperature phase has a fcc structure.[2] Slow cooling from high temperature leaves the system in the ortho-I structure, whereas a rapid quench yields another orthorhombic phase (called ortho-II).[8,9] This latter structure is metastable, converting to ortho-I with a relaxation rate depending on temperature; below 200 K, however, the relaxation rate is negligible.[10] There is strong evidence that the ortho-I phase consists of covalently bound polymers and the ortho-II consists of dimers.

We have studied stoichiometrically pure RbC$_{60}$ by differential scanning calorimetry (DSC) and infrared spectroscopy during temperature cycles that yielded all three structures. Detailed accounts of our investigations will be presented separately. In this paper, we concentrate on the characterization of a phase emerging between 270 and 300 K. We observe this phase (or probably a sequence of two phases) when quenching to 273 K from 450 K and also when warming the ortho-II phase from 77 K, before the ortho-I structure appears. Its infrared spectrum indicates that the C$_{60}^-$ anions are present as monomers. The results can be explained by assuming that the phase transitions involve the breaking and formation of chemical bonds and thus support the polymerization picture for the ortho-I phase.

RbC$_{60}$ was prepared by the solid state reaction of stoichiometric quantities of Rb and sublimed high purity C$_{60}$ powder. X-ray diffraction proved it to be pure 1:1 RbC$_{60}$ consisting only of the ortho-I phase. The phase transformations were followed by a Perkin-Elmer DSC-2 calorimeter. We used a Bruker 113v Fourier-transform

spectrometer to measure the infrared transmittance of the powder pressed in KCl pellets. A flow cryostat allowed the sample to be cooled to low temperatures or heated to temperatures above 425 K.

The DSC results are summarized in Fig. 1. We began our investigation after quenching the material from 500
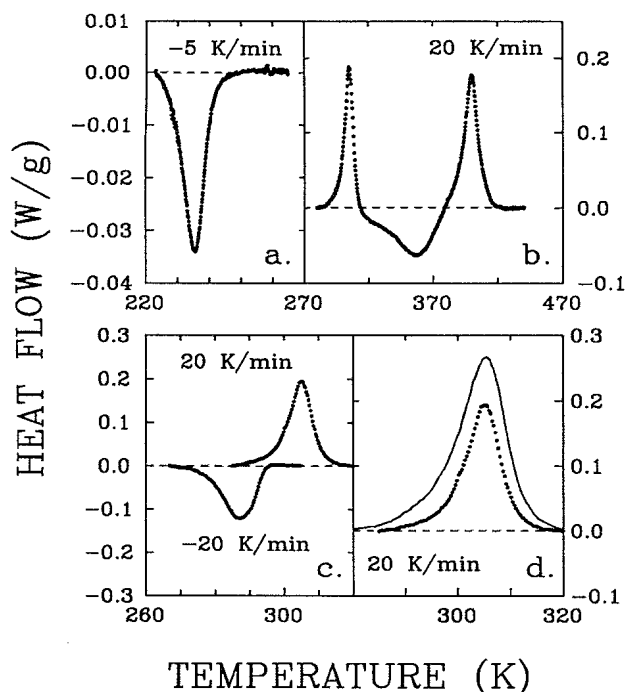

FIG. 1. DSC thermograms for RbC$_{60}$. (a) Cooling after quenching to 273 K. (b) Heating after quenching to 273 K. (c) Reversibility of the endothermic peak above 273 K. (d) The endothermic peak above 273 K: dotted line—after quenching to 273 K; solid line—after quenching to 215 K and cycling between 215 and 273 K.

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K to 273 K. Earlier x-ray diffraction experiments showed that the 273 K quenched sample has a cubic structure.[6] This is termed as fcc in Ref. 6, although the 2Θ range does not allow the distinction of fcc and simple cubic (sc) structures. Rapid cooling from this phase results in the dimerized ortho-II phase.[8,9]

The DSC thermogram recorded on cooling below 273 K shows an exothermic peak at 235 K [Fig. 1(a)] which we associate with the cubic → ortho-II transformation. If, however, the quenched cubic phase is warmed above 273 K, an endothermic transition is observed [onset at $\sim$285 K, peak temperature 305 K, Fig. 1(b)] that overlaps with the formation of the ortho-I phase (the broad exothermic process peaked at 360 K). The endothermic process is reversible so far as the ortho-I fraction is negligible [Fig. 1(c)]; otherwise, a reduced peak area is observed on cooling. The enthalpy of transformation (4.8 kJ/mol) is comparable to that expected for the onset of rotation of the C_{60}^- ions (3/2RT=4.0 kJ/mol at 320 K). These features are consistent with a rotational transition similar to that observed at 250 K in pure C_{60}. If so, an orientationally ordered cubic (probably sc) phase exists below 285 K, and a freely rotating fcc phase is expected for $T >$285 K. Above 380 K, another endothermic reaction takes place, which corresponds to the ortho-I → fcc transition seen earlier in fully polymerized (ortho-I) samples.[2] The peak area is, however, smaller, which indicates that on the time scale of the DSC experiment the polymerization was incomplete.

The ortho-II structure is also produced when quenching directly to lower temperature.[9] The DSC thermogram recorded after such treatment is similar to that in Fig. 1(b), except that the endothermic peak at 305 K becomes higher and broader [Fig. 1(d)]. The excess peak area is comparable with that of the cubic→ortho-II transition. We assign this peak to the decomposition of the ortho-II phase. At about 320 K, this process is completed and the formation of the ortho-I phase has just started. These results give strong evidence for the presence of a distinct structure that forms as a transient state between ortho-II and ortho-I.

The room-temperature cubic phase has been identified in KC_{60} when warming from ortho-II, but in the rubidium salt only a mixed phase was seen.[9] However, the presence of the same chemical species in the room-temperature cubic phase as in the high-temperature fcc phase can be confirmed independently by infrared spectroscopy. Temperature treatment in this case consisted of elevating the temperature of an ortho-I phase sample to 425 K, where the structure is fcc, followed by rapid quenching with liquid nitrogen, yielding the ortho-II (dimer) phase. This sequence of steps yielded reference spectra of the three known phases. These agree basically with those measured by Martin and co-workers on films[10,11] and KBr pellets,[12] but do not contain either Rb_6C_{60} or silicon lines. The principal lines and their temperature dependence correspond to those obtained by Pichler et al.[13] and Winkler et al.,[14] using infrared reflectivity on films and crystals. For identification, we use the vibrational structure in regions containing unique features of the individual phases. We show

transmission curves (relative to KCl pellets at the same temperature) in these areas in detail in Fig. 2. The absolute transmission scale in the three panels of the figure is shifted because of the sloping baseline, but the curves themselves have not been displaced relative to each other. The change in baseline reflects the electronic background, which is distinctly different in the three phases, decreasing in the order ortho-I → fcc → ortho-II. This trend follows the dc conductivity, but we do not attribute it directly to free electrons. The optical conductivity of ortho-I RbC_{60} crystals[15] has been described by a Drude-Lorentz model with a very narrow ($\Gamma < 100$ cm^{-1}) Drude contribution and a broad midinfrared band; we believe that the latter is dominant in the region investigated here.

The sample was slowly warmed up from 77 K and kept between 270 and 290 K, while infrared measurements were performed. Subsequently it was requenched to 77 K and measured again; after which it was warmed to room temperature and allowed to relax for several hours prior to measuring the final spectra. The heating rate above 200 K was less than 1 K/min, therefore the temperature scale differs somewhat from that of the DSC experiment.

Figure 3 illustrates the evolution of the spectra during these latter steps. Since we concentrated here on thermal changes, no KCl reference spectra were taken; thus, background intensities are arbitrary and curves have been shifted for clarity rather than reflecting true relative intensities. For the same reason, outgassing in the cryostat was not totally compensated for, causing extrinsic lines to appear at 810 and 1230 cm^{-1} in Fig. 3.

Quenching from 425 K to 77 K yielded the ortho-II phase (with a small admixture of C_{60} formed at high temperature). On a subsequent warmup, the ortho-II phase remained dominant, with spectra like the upper traces of Fig. 2, so long as the temperature was below 270 K. Continued warming above 270 K caused the spectrum to lose the characteristic features of ortho-II and to become similar to the fcc phase, showing only the four T_u modes. This is illustrated by the top trace of Fig. 3. If we requench from 290 K to 77 K, the typical lines of the ortho-II phase (815, 837, and 1309 cm^{-1}) reappear (see the middle spectrum of Fig. 3), although with less intensity than when quenched from high temperature. In addition, some ortho-I lines become distinguishable, the strongest being the 1388 cm^{-1} shifted $T_u(4)$ mode. However, the biggest change in the second quench is the reappearance of the ortho-II lines. Letting the sample warm up to room temperature from either quenched phase yields, after a short time, the ortho-I spectrum. Cooling, either rapid or slow, does *not* produce any sign of the characteristic ortho-II spectrum again.

There are basically two approaches to the structure of the various 1:1 RbC_{60} phases. One can regard them as consisting of only slightly distorted individual C_{60}^- molecular ions, the distortion being determined by the crystal structure.[16] In this picture, infrared spectra should reflect the symmetry of the lattice in their second-order structure, but the main features should still be those of the C_{60}^- molecular unit. If, however, the orthorhombic phases consist of molecular entities formed
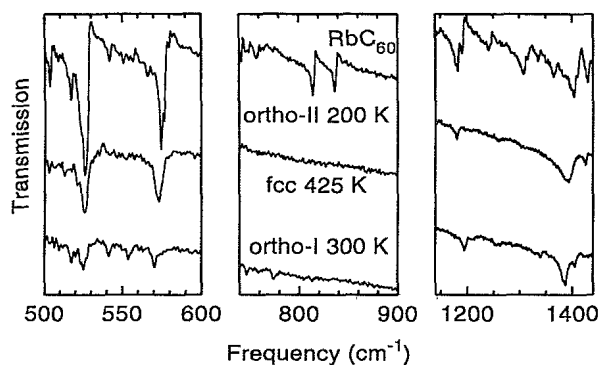
FIG. 2. Infrared spectra in selected regions of pure fcc, ortho-I, and ortho-II phases.

by C_{60}^- balls connected via covalent bonds, then the molecular symmetry changes and new first-order lines are expected. In this case, the driving force behind the phase transition is the chemical reaction forming or breaking those bonds. The latter view is supported by both x-ray diffraction and vibrational spectroscopy. Oszlányi et al.[9] observed a strongly reduced ball-to-ball distance in the dimer phase. Martin et al.,[11] by comparing infrared and Raman lines, found that in the orthorhombic phases, the C_{60}^- molecular ions have undergone transformations that lower their molecular symmetry. Our findings endorse the explanation put forward by these authors, namely, that chemical bonds are formed between two neighboring balls (ortho-II) or connecting several balls in a one-dimensional chain (ortho-I). Depending on the kinetics, these bonds represent either a stable formation[17,5] or a metastable one, where only two molecules can enter into bonding. When the metastable phase begins to relax, monomers are again formed in the first step. Quenching from this point freezes the mixed phase and both dimers and polymers are distinguishable.

The infrared spectrum of C_{60} and its derivatives reflects their molecular structure rather than the long-range order in the crystal. First-order spectra of pristine
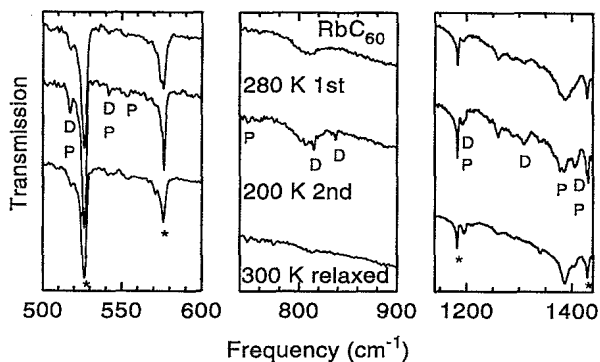

FIG. 3. Spectra during temperature cycling. From top to bottom: warmed from ortho-II at 77 K to 290 K; requenched from 290 K to 77 K; slowly warmed to 300 K. The peaks labeled P are indicative of the polymer, while those labeled D correspond to the dimer phase. Absorption lines due to pristine C_{60} are indicated by asterisks.

C_{60} are known to be almost identical in the gas phase, solution, or solid state. When going through the rotational transition, splitting of the principal lines in crystalline C_{60} has been detected by high-resolution infrared spectroscopy.[18] Also, second-order effects have been observed in both infrared[19] and Raman[20] spectra, giving rise to numerous bands about an order of magnitude weaker than the allowed T_u vibrations. Such changes are not distinguishable in our present spectra of relatively thin polycrystalline specimens. Therefore, we cannot tell apart the two cubic phases (orientationally ordered and freely rotating fcc) expected on the basis of the DSC results. We can, nevertheless, clearly identify by infrared means a point in the relaxation process where monomers comprise the majority. This observation also indicates that the interball bonds involve different atoms in the dimers and polymers. The molecular orientation in the ortho-II phase cannot be unambiguously deducted from available x-ray data and several possibilities have been suggested.[9] One of these is analogous to what was proposed for dimers formed during photopolymerization,[17] i.e., two balls connected via 2+2 cycloaddition. Such dimers could polymerize directly, without any need for molecular reorientation. If, on the other hand, the molecular ions have to assume a different geometry before the polymerization takes place, one can explain the formation of monomers.

If the fcc → ortho-I transition were driven entirely by structural factors, e.g., the rotational freezing of the balls, then it is very unlikely that one can produce the ortho-I phase from the same structure both by warming from 270 K and by cooling from 425 K. The presence of monomers as intermediates in the dimer-to-polymer transition also contradicts the picture of this transformation as a Peierls transition.[8] In our view, the process starts with the breaking of interdimer bonds, followed by a rotation of the monomers into positions favorable for the polymerization reaction, and finally the cycloaddition. The electronic system in such a reaction changes in a far more complicated way than in a Peierls model.

Other cubic phases have also been identified in AC_{60} salts (A = K, Rb, Cs): an intermediate fcc phase in KC_{60} around 400 K (Refs. 2 and 21) as well as a low-temperature primitive cubic structure in CsC_{60} and RbC_{60}.[22,23] In our particular temperature sequences, we did not detect these phases. Based on ESR and calorimetric data, Kosaka et al.[23] recently suggested that the decomposition of the ortho-II phase follows the sequence ortho-II → orientationally ordered → fcc → ortho-I. Considering the different heating rates, our results are not inconsistent with this picture. Structural and spectroscopic studies are underway to clarify this issue and to further characterize the transient cubic phases.

In conclusion, we have followed the various structural transitions in RbC_{60} by differential scanning calorimetry and infrared spectroscopy and identified a room-temperature cubic phase during relaxation of the metastable ortho-II to the stable ortho-I phase. Our results, together with structural evidence, support the picture of solid-state chemical reactions driving the phase transitions. After submitting this manuscript, we be-

came aware of the work of Petit, Robert, and Fischer,[24] who identified the room-temperature cubic phase in KC_{60} by ESR spectroscopy.

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