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Ordered low-temperature structure in K_4C_{60} detected by infrared spectroscopy

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Infrared spectra of a K_4C_{60} single-phase thin film have been measured between room temperature and 20 K. At low temperatures, the two high-frequency T_{1u} modes appear as triplets, indicating a static D_{2h} crystal-field stabilized Jahn-Teller distortion of the $C_{60}{}^{4-}$ anions. The $T_{1u}(4)$ mode changes into a known doublet above 250 K, a pattern which could have three origins: a dynamic Jahn-Teller effect, static disorder between "staggered" anions, or a phase transition from an orientationally ordered phase to one where molecular motion is significant.

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The electronic structure of fulleride salts has been a topic of intense interest since their discovery. Three recent reviews summarized the situation: Reed and Bolskar[1] focused on isolated ions; Forró and Mihály[2] treated fulleride solids; and Gunnarson[3] concentrated on the theory of superconductivity and on band-structure calculations, including the important concepts of the Jahn-Teller (JT) effect.[4] Fulleride anions with charges other than 0 or 6 are susceptible to Jahn-Teller coupling between electrons occupying partially filled t_{1u} orbitals and H_g phonons. Because of the high degeneracy of the phonons involved, the coupled electronic Hamiltonian acquires an SO(3), higher than the original icosahedral configuration.[5] Thus the electronic structure of the outer shell can be discussed in complete analogy with *p* electrons on an atom.[2] In any uniaxial crystal field, one expects a twofold orbital splitting to e_{2u} and a_u, whereas in a biaxial system the degeneracy is completely lifted, resulting in three distinct electronic levels. [It follows from the SO(3) symmetry that the principal axes of the distortions can be taken as the axes of the crystallographic unit cell, regardless of the position of the molecule within the crystal.]

In solids the orbital splitting is small compared to the bandwidth; thus electron correlation has to be taken into account. The most comprehensive theoretical treatment of this interplay was given by Fabrizio and co-workers, who introduced the concept of the "Mott-Jahn-Teller insulator" (M-JT).[6,7] The model of *p*-like electrons on a spherical or ellipsoidal surface was indeed succesful in the interpretation of NMR,[8,9] photoelectron spectroscopy,[10,11] resonance Raman,[12] and magnetic[13] data. The situation becomes different, however, once we try to measure properties that reflect the internal degrees of freedom within the C_{60} ball itself. Typical examples are magnetic resonance measurements and vibrational spectroscopy. When atomic motion has to be taken into account, the symmetry can no longer be regarded as spherical. Instead, the actual shape of the molecule is determined by the combined internal (JT) and external (crystal field) distorting forces. If these result in a potential surface with several shallow wells, then the balls will assume different shapes and positions with respect to the lattice. The result will be either static disorder or random fluctuations between the minima, called the dynamic Jahn-Teller effect.

A special frustration results if the principal axis of the crystal system does not coincide with a similar molecular axis. The case of A_4C_{60} salts[14] is such an example. These show peculiarities in both their crystal structure and vibrational spectra. At room temperature, K_4C_{60} and Rb_4C_{60} form a bct crystal,[15] with merohedral disorder similar to that in A_3C_{60}:[16] in the bct cell of K_4C_{60} there is only a C_2 molecular axis in the *c* direction, and the overall tetragonal structure is realized by the anions occupying two standard orientations with equal probability. In Cs_4C_{60} an orthorhombic distortion was found at room temperature,[17] resulting in a lattice compatible with D_{2h}, one of the subgroups of the icosahedral group yielding complete ordering of the C_{60} balls.

Infrared measurements on K_4C_{60} and Rb_4C_{60} at room temperature by Iwasa and Kaneyasu[18] found the $T_{1u}(4)$ infrared active mode to be split into a doublet, a phenomenon not seen in any other alkali salt so far (excluding polymeric forms, which show a variety of splitting patterns). They invoked a static JT distortion to explain these results. X-ray diffraction[15] puts an upper limit of 0.04 Å on the difference between the polar and equatorial radii of C_{60} (the polar direction supposed to lie in the crystallographic *c* direction). To our knowledge, neither structural nor vibrational properties of A_4C_{60} salts have been reported at low temperatures.

Details concerning the temperature dependence of the molecular dynamics in A_4C_{60} salts were provided by nuclear magnetic resonance studies.[8,9,19,20] Goze *et al.*[20] observed that four ^{13}C NMR lines in Cs_4C_{60} collapse into a single line above 350 K, the latter spectrum being similar to K_4C_{60} at room temperature.[19] Lacking structural data, they could not draw unambigous conclusions, but they invoked the possibility of a phase transition between ordered and rotationally disordered phases and even suggested that a similar transition may take place in other tetravalent alkali salts at lower

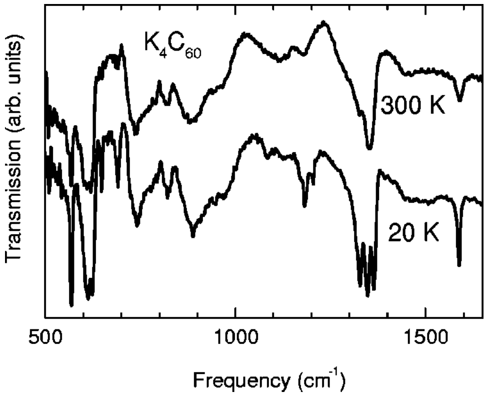

FIG. 1. Infrared spectra of a K_4C_{60} layer on silicon in the entire midinfrared range at 20 and 300 K.

temperatures. Comparing the NMR results with high-quality room-temperature x-ray-diffraction data obtained on K_4C_{60} and Rb_4C_{60} (which are isostructural)[15] and Cs_4C_{60},[17] it seems highly possible that a phase transition occurs in all three salts, above room temperature in Cs_4C_{60} and below in the other two. Due to its sensitivity to local symmetry, infrared vibrational spectroscopy should be a good indicator of such a transition. Therefore, we undertook infrared spectroscopic measurements between 20 and 300 K in K_4C_{60}.

Highly polycrystalline films of C_{60} were grown on Si IR windows using a "hot-wall" technique.[21] We estimate a thickness of 300 nm from the spacing of interference fringes in the infrared, assuming an index of refraction $n=2$. A glass and metal doping cell was constructed incorporating a potassium source and ZrO getter (SAES Getters/ USA Inc.), replicating earlier preparations from Bell Labs.[22] The cell was thoroughly outgassed at 300 °C, and sealed at a base pressure of 10^{-7} torr. During doping the cell was kept at 200 °C and the resistance was monitored. The minimum resistance corresponding to K_3C_{60} was observed and the time required to reach K_4C_{60} composition estimated. Then the sample was transferred in an Ar-filled glovebox into a copper holder and epoxied in place.

Spectra were taken in the midinfrared by a Bruker IFS28 Fourier-transform infrared spectrometer with a mercury cadmium telluride (MCT) detector and in both the far and midinfrared by a Bruker IFS113v instrument using a Si bolometer and a deuterated triglycine sulphate (DTGS) detector, respectively. The temperature dependence was measured in a He flow cryostat while warming up, to avoid possible hysteresis effects. Although the measurements were taken in a reflection mode with the silicon window facing the incident light path, our results are essentially transmittance data. This is because the experimental arrangement resulted in the light passing through the silicon window and the sample film twice, once on entering the sample and a second time after being reflected from the copper back plate. Because we were mainly interested in the change in spectral line positions, we did not undertake any correction for reflection from the silicon window, and assumed 100% reflection from the copper.

Figure 1 shows the infrared spectrum of the film at 300 and 20 K. The 300-K spectrum is identical to that measured by Iwasa and Kaneyasu,[18] the most pronounced feature being the asymmetric doublet at 1323 and 1353 cm^{-1}. The $T_{1u}(3)$ mode at 1177 cm^{-1} is broader than that in other fulleride salts, but shows no explicit splitting. Neither of these peaks coincides with infrared vibrations of other fulleride ions; moreover, characteristic peaks of other fulleride ions are absent, giving evidence of the phase purity of the film. The low-frequency T_{1u} mode region is obscured by multiphonon Si absorption occurring between 570 and 700 cm^{-1}, therefore we concentrate on the high-frequency region, where neutral isolated C_{60} has two (triply degenerate) normal modes at 1183 and 1429 cm^{-1}. In Fig. 2, this part of the spectrum is depicted at 20, 200, and 300 K. An obvious change occurs between 300 and 200 K; at 20 K the structure becomes sharper, but otherwise the spectrum is identical to that at 200 K. At our heating rate of 2 K/min, we observed this change between 250 and 260 K. The two high-frequency T_{1u}modes both evolve into a triplet below this temperature (one set at 1168, 1184, and 1206, and another at 1327, 1347 and 1364 cm^{-1}).

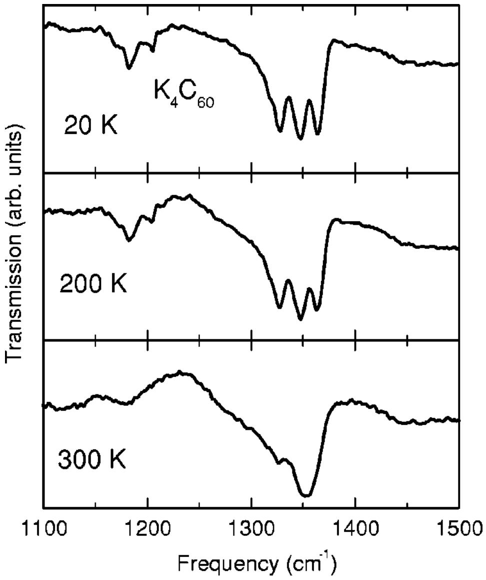

FIG. 2. Infrared spectra of K_4C_{60} in the region of the high-frequency C_{60} molecular vibrations, at three different temperatures.

The threefold splitting in the T_{1u} peaks is a clear signature of biaxial symmetry, a complete lifting of the threefold degeneracy in the vibrational levels. A straightforward explanation is the existence of an ordered crystal structure at low temperature, similar to that of Cs_4C_{60}.[17] There, the site symmetry of the balls is D_{2h}, a direct subgroup of I_h. This subgroup is also special in the sense that it can describe one possible shape of a JT distorted icosahedral molecule, resulting from linear coupling between t_{1u} electrons and H_g phonons.[4] The principal axis of the point group coincides with that of the crystal space group; thus all the conditions for a crystal-field-stabilized static JT distortion are met. We conclude that the likely explanation for the low-temperature infrared spectrum of K_4C_{60} is such a structure.

It is not straightforward to interpret the spectrum at 300 K, where the structure is known. If we assume a static merohedral disorder with appropriate JT distortion, then molcecules with different standard orientations should give the vibrational spectrum of the local symmetry D_{2h}, and thus should not differ from the low-temperature spectra. Because the spectra do differ, we suggest that either the molecules are trapped in more complicated orientations (the ‘‘staggered static distortion’’ introduced by Fabrizio and Tosatti[6]), or that dynamical processes are involved. The two allowed distorted point groups for t_{1u}-H_g coupling, besides D_{2h}, are D_{3d} and D_{5d}. The principal axes of these two distorted symmetries go through the center of the hexagonal and pentagonal faces of the C_{60} molecule, respectively. The staggered static distortion would have neighboring anions with principal axes different from *c*, but symmetric around it; no experimental corroboration of this idea was reported. It is interesting to compare the measured upper limit for the static distortion, 0.04 Å ,[15] with the only hitherto known C_{60} distorted structure, that of $C_{60}{}^{2-}$ in $(PPN)_2C_{60}$.[23] (The JT coupling in this ion is supposed to be very similar to the tetravalent anion, because they are related by electron-hole symmetry.) There, a distortion of 0.033 Å was enough to produce a split EPR signal in accordance with symmetry lowering of the anion,[31] but the point group was C_i, lower than that predicted by the JT effect alone (due to the complicated organic counterions), and involved a considerable D_{5d} character, pointing to a D_{5d} distortion stabilized by crystal-field effects and locked into a configuration with even lower symmetry.

In the case of K_4C_{60}, however, the C_3 axes seem more special. We first consider their role in A_3C_{60}, which adopts a remarkably similar molecular arrangement in the *ab* plane[16] with two standard orientations, connected formally by a 90° rotation around the *c* axis. In $Rb_3C_{60}$and $K_3C_{60}$the rearrangement between the two standard orientations can also occur through a 44.5°jump around a C_3 axis, lying in the crystallographic $\langle 111 \rangle$ direction, and it has been shown by neutron-scattering experiments that this motion involves a considerably lower-energy barrier than the jump around C_2.[24] Subsequent NMR studies[25,26] indicated that a fast uniaxial rotation takes place around a fixed axis, accompanied by a slow motion which was interpreted as a flipping of the molecule while keeping the same rotational axis. The existence of fast and slow reorientational motions was also reported in A_4C_{60}.[8,19] If one invokes the special role of the C_3 axes, then it is possible that the easy rotation around this axis lowers the energy of the D_{3d} distortion over both D_{5d} and D_{2h}.

At this point, we turn to the description by Chancey and O’Brien[4] of the dynamical Jahn-Teller effect in C_{60}. They introduced the concept of ‘‘pseudorotation,’’ a succession of symmetry-allowed distortions progressing on the surface of the ball, causing a continuous change in the shape of the molecule without effectively rotating it. Comparing this model to that of the motions deduced from NMR spectroscopy, we can associate the axial rearrangement with such a pseudorotation (obviously, a genuine rotation should involve changes in the positions of atoms, because it takes the molecule from one standard orientation to another). This motion should go through distorted states which mainly involve axial components (D_{3d} and/or D_{5d}), and can be considered as the dynamic equivalent of the staggered state proposed by Fabrizio and Tosatti.[6] Based on vibrational spectra, it is not possible to distinguish between the dynamic process and the staggered state, so long as biaxial (D_{2h}) distortions are not involved; both the spatial and time averages of uniaxially distorted states would give a twofold line splitting. The transition between the low- and high-*T* states, however, would be different in the two cases. A staggered tetragonal phase can only evolve from an ordered structure through a structural phase transition. Such a transition could, of course, also occur between an ordered phase and a dynamically disordered phase, as in pristine C_{60}, but it is also possible that a disordered state develops from an ordered one by the rotational frequencies increasing above a critical value. The first case should lead to a discontinuity at the transition temperature observable by any spectroscopic method, regardless of the time scale; the second scenario would give different transition temperatures depending on the time scale of the experiment relative to the autocorrelation time of the motions.[27] From the parameters given by Zimmer *et al.*,[19] the autocorrelation time τ is 33 ns at 200 K and 1 ns at 300 K, which can be regarded as static on the time scale of molecular vibrations. The same calculation for the fast uniaxial rotation gives 71 ns at 200 K and 130 ps at 300 K, still too slow to cause collapsing of infrared lines. (In C_{60}, $\tau = 64$ ns at 200 K, below the structural phase transition,[29] where infrared lines are observably split,[30] and 12 ps at 300 K, in the rotator phase, where there is only a single infrared peak per T_{1u}mode.) We therefore conclude that the temperature evolution of the infrared spectra cannot be explained by simple activated behavior of some molecular motion; rather, an abrupt phase transition has to occur to a state where the rotations are faster. Suggestions for a phase transition were put forward by Goldoni *et al.*[28] based on an anomaly in the C-1*s* photoemission linewidth below 150 K, which they correlated with the peak in the NMR spin-spin relaxation time,[19] and attributed to the stopping of the slow reorientational motion. We find this suggestion difficult to reconcile with the results presented here, in part because our transition temperature is higher than 150 K, and in part because the splitting of IR lines should be related to the fast motion rather than the slow reorientation.

More structural and spectroscopic data are clearly needed on fulleride salts to fully understand their intriguing behavior. In addition, vibrational spectra of isolated ions could tell whether the splitting at either high or low temperature is caused by an inherent molecular JT distortion or by a crystal-field effect brought about by the surrounding cations. Indirect proof of a molecular distortion comes again from studies[31] on $C_{60}{}^{2-}$, where the same EPR structure was found in the PPN crystal and in frozen solution, indicating that the effect of crystal structure was not dominant. Therefore, we think it possible to have a D_{2h} configuration in the low-temperature state and a combination of the two axially distorted forms, D_{5d} and D_{3d}, connected by a pseudorotation, in the high-temperature state.

In conclusion, we observed a change in the $T_{1u}(3)$ and $T_{1u}(4)$ infrared-active vibrations of C_{60} in K_4C_{60} from doublet to triplet in the 200–300-K range. We propose a structural bct-to-orthorhombic transition to take place in this region.

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