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Dimerization in KC_{60} and RbC_{60}

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An orthorhombic phase of KC_{60} and RbC_{60} is found below 270 K in samples quenched through the fcc-to-polymer phase transition. X-ray diffraction, ESR, and dc conductivity measurements establish the formation of covalently bonded dimers in the solid state. The phase has an insulating diamagnetic ground state but becomes paramagnetic above 220 K.

In the short time since the discovery of C_{60}, an amazing variety of compounds have been found. In most of them the intermolecular separation is mainly determined by van der Waals interactions and the structure of the C_{60} molecule is hardly distorted from the truncated icosahedron. The center-to-center distance of C_{60} molecules is typically 10 Å, and often they are orientationally disordered at high temperatures. Recently some exceptions have been found in which C_{60} molecules are linked by covalent bonding in the solid. Pure C_{60} polymerizes under light[1] and also under pressure at high temperatures.[2] AC_{60} with A=K, Rb have a polymeric form[3–5] below about 400 K with an orthorhombic crystal structure,[6,4] in which C_{60} molecules are bonded into parallel charged chains. At ambient temperature the polymeric AC_{60} phase has a large spin susceptibility χ,[7,6] and is electrically conducting.[8] AC_{60} transforms reversibly in the solid state between the orthorhombic phase[6] and a high temperature monomeric state which has a rocksalt (fcc) structure.[9]

The polymerization of AC_{60} may be prevented by a rapid cooling of the monomeric fcc phase to low temperatures. ESR experiments[7] showed that a new compound is formed by quenching fcc RbC_{60} from 500 K to temperatures below 270 K. An unusual temperature dependence of the spin susceptibility[6,7] has been found in the quenched state. Optical studies[10] showed that quenched RbC_{60} is an insulator at low temperatures. At ambient temperatures it transforms into polymeric RbC_{60} within a few hours. In this paper we present new magnetic susceptibility, dc electrical conductivity, and x-ray structural data of KC_{60} and RbC_{60}. A recent structural study of quenched KC_{60} by Zhu *et al.*[11] showed that the quenched state at low temperatures is orthorhombic (ortho-II), in which the C_{60} ions form chains with alternating longer and shorter center-to-center separations. We have independently reached the same conclusions.

Neither x-ray study has yielded an atomic-level structure showing whether the dimers are linked by covalent bonds, or how the fullerenes are oriented in the lattice. We therefore take the approach of integrating the x-ray, conductivity, and susceptibility data to obtain whatever information is possible about the nature of the quenched phase. In particular, Zhu *et al.*[11] have described the existence of dimers in this phase as a Peierls distortion, i.e., a small elastic distortion driven by the opening of a gap in a quasi-one-dimensional electron spectrum. We argue instead that the structure consists of covalently bonded $(C_{60})_2$ molecules.

The polycrystalline powder samples of KC_{60} and RbC_{60} were prepared by the solid state reaction of stoichiometric amounts of alkali metals and high purity (99.9 %) C_{60} powder at 650 K. The same samples were used for x-ray and ESR spectroscopy. Parallel beam x-ray diffraction spectra were recorded at the X3B1 beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. The powder samples were phase pure in the sense that only fcc AC_{60} was observed in x-ray diffraction at 470 K, only the orthorhombic polymer phase was observed at room temperature, and no signature of superconductivity (by A_3C_{60}) was observed in the susceptibility. However, in the quenched samples, a small amount of fcc AC_{60} coexisting with the majority ortho-II phase was always observed. The spin susceptibility was measured by appropriately integrating the ESR line. dc resistivity of KC_{60} and RbC_{60} was measured *in situ* on single crystals grown in sealed Pyrex tubes. The platinum electrodes were contacted to the crystals with silver paste. Doping was performed at 480 K and the resistance was monitored during the doping. The temperature dependence of the conductivity showed only negligible amounts of the superconducting phase in the single crystals: the superconducting transition is not observed at all in the quenched phase. The temperature dependence of the dc resistivity of several doped single crystals was the same.

The spin susceptibility of KC_{60} and RbC_{60} powders in the high temperature monomeric fcc phase and the quenched phase is shown in Fig. 1. The high temperature data are taken by cooling from 800 K to 380 K. The low temperature data are taken on heating after a quench from 500 K to helium temperatures within a few minutes. Once the sample has been cooled to low temperatures there is no hysteresis in the susceptibility of the quenched state, as long as the temperature was maintained below 280 K. Above that temperature, the sample begins to convert to the paramagnetic conducting polymer phase, and so it is no longer possible to follow the susceptibility back to its 200 K baseline. No data are shown in the temperature range of 300 K to 380 K, where only the polymeric phase is observed. The monomer rocksalt phase has a large paramagnetic susceptibility which decreases roughly as $1/T$. Electrons are localized onto C_{60} ions although some overlap remains between neighboring sites, and at 500 K the absolute value of χ is less by 20% than its value for noninteracting 1/2 spins. Below 220 K, $\chi(T)$ of the quenched phase is characteristic of a diamagnetic insulator with about 1% of localized impurity spins. Above 220 K the susceptibility of the quenched phase increases dramatically, and, as noted above, without hysteresis.

Typical dc resistivity curves of KC_{60} and RbC_{60} single crystals in the 100–500 K temperature range are shown in Fig. 2. In the fcc phase at high temperatures, both compounds show activated conductivity with a small gap of $2\Delta=0.1$ eV.

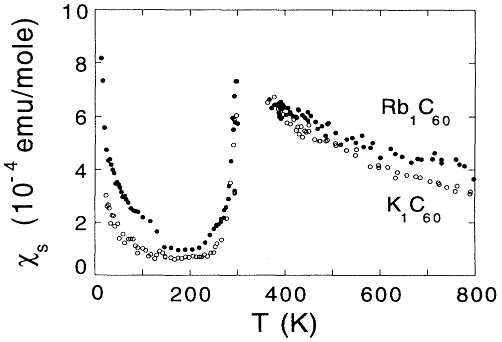

FIG. 1. Spin susceptibility of KC_{60} and RbC_{60} in the monomeric rocksalt phase above 400 K and in the quenched phase below 300 K.

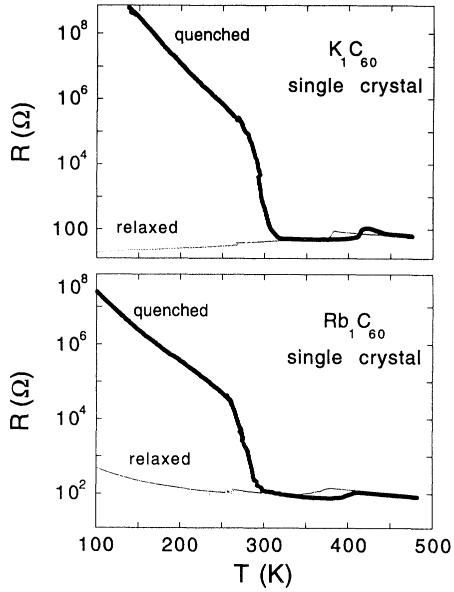

FIG. 2. dc resistivity of KC_{60} and RbC_{60} single crystals doped at 480 K. The *R-T* curves with the "relaxed" label were measured on slow cooling, while curves with the "quenched" label were measured on heating after the samples were quenched from 480 K to a 100 K.

Curves labeled "quenched" correspond to samples rapidly cooled from 500 K to below 100 K and measured on heating. Like the susceptibility, the resistivity is reproducible as long as the temperature is maintained below 280 K. The resistivity of the quenched state indicates that it is an insulator at low temperatures with an energy gap of $2\Delta=0.3$ eV in KC_{60} and $2\Delta=0.2$ eV in RbC_{60}.

The curves labeled "relaxed" correspond to samples cooled slowly from 500 K. The polymerization-depolymerization transformation is well identified by a hysteretic loop in the resistance. Polymeric KC_{60} is metallic as expected from the static susceptibility. In the temperature range shown, polymeric RbC_{60} has a slowly increasing resistance with decreasing temperature, suggesting that it has an insulating ground state in agreement with an imperfect quasi-one-dimensional conductor with a spin density wave ground state as suggested in Ref. 6. A detailed account of the conductivity in the polymeric state will be given elsewhere.[8]

X-ray diffraction patterns were taken in the quenched state in the 50–300 K range after quenching from 500 K into liquid nitrogen; that shown in Fig. 3 (240 K) is typical. All but a few low angle peaks (indicated by arrows in Fig. 3) can be indexed to a body-centered orthorhombic cell of dimensions a=9.61 Å, b=9.79 Å, c=14.19 Å for KC_{60}, and a=9.63 Å, b=9.92 Å, c=14.15 Å for RbC_{60}. This bears the same relationship to the high temperature fcc cell as does the polymer phase (9.13 Å×10.11 Å×14.23 Å). In both cases the orthorhombic structure is obtained by compressing the fcc cell along the [110] direction. The compression for the present cell

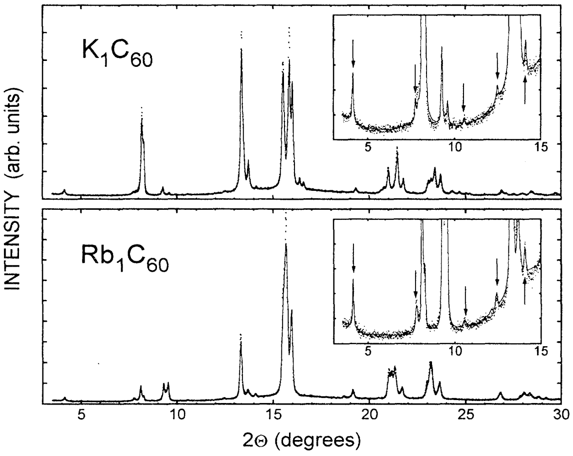

FIG. 3. X-ray diffraction pattern of KC_{60} and RbC_{60} at 240 K (λ=1.1490 Å). Dots are experimental data and the solid curve is a Rietveld fit using the spherical shell approximation for the scattering factor of the C_{60} molecules. Insert: the region of superreflections marked by arrows is magnified.

is roughly half that of the polymeric ortho-I structure, which suggests that half of the fullerene pairs are bonded and the bonding is along **a**. The few low angle peaks can be indexed with half-integer indices for h and l, implying that the cell is doubled along the **a** and **c** directions. The doubling along **a** is easily understood as an alternating pairing of fullerenes along that axis, and that along **c** as an indication that the dimer pairs alternate along **c**, with the possibility of some accompanying relaxation. Figure 4 illustrates this geometry. The supercell diffraction peaks occur only at low angles, therefore they could not be due to orientational ordering of the C_{60} molecules.

Based on its dimensions, this enlarged cell contains eight fullerenes, and so it is important to discover what symmetry relations connect them. We will use primes to denote quantities pertaining to the doubled orthorhombic cell. The fact that h' and l' are both odd for the five supercell reflections suggests that the large cell is B centered ($h'+l'$ even). However, the body-centering symmetry element of the small cell ($h'/2+k'+l'/2$ even) does not appear as a symmetry element in any orthorhombic space group for the large cell. Furthermore, the required relaxation of the fullerenes at $(x,1/2,1/4)'$ in parallel with those at $(x,0,0)'$ is not compatible with orthorhombic symmetry. This leads us to consider, following Zhu *et al.*, a C-centered monoclinic cell with dimensions $a_{\rm mono}=\sqrt{({a'_{\rm ortho}}^2+{c'_{\rm ortho}}^2)/2}=17.14$ Å, $b_{\rm mono}=b'_{\rm ortho}$, $c_{\rm mono}=a'_{\rm ortho}$, and $\beta_{\rm mono}=-\arctan(c'_{\rm ortho}/a'_{\rm ortho})=124.11^\circ$. Note that there is no obvious symmetry requirement fixing this relationship among the four independent monoclinic lattice parameters. It remains an important unsolved issue to understand why the monoclinic cell so closely mimics an orthorhombic one in the sense described here.

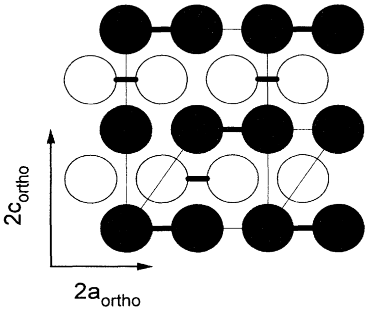

FIG. 4. The ac projection of the 2a,b,2c supercell showing only the position of the C_{60} molecules and the dimer bonds between them. The true monoclinic unit cell is also outlined.

The magnitude of the modulation may be estimated from the intensities of superlattice reflections. These are not sensitive to the orientation of the C_{60} molecules. In the low-q region the scattering factor of the C_{60} molecules may be approximated by a spherical shell charge distribution. The superreflection intensities clearly indicate a dimerization along **a** and a small tilt around the b axis as described by Zhu.[11] Superreflections in both KC_{60} and RbC_{60} are well described with the same fractional coordinates. The interfullerene distance within the dimer is 9.34 Å, the interdimer distance is 9.9 Å and the dimers are tilted by 1° around their center in the ac plane. This "spherical fullerene" model gives a weighted profile R factor, $R_{\rm wp}=12\%$ for KC_{60} and $R_{\rm wp}=10\%$ for RbC_{60}. We have not been able to find any atomic decoration of the fullerene shell that gives a significant improvement to these fits.

It has been noted in IR experiments that the dimer phase transforms into a conducting phase, presumably the polymer, through an activated process.[10] The characteristic time of this process is dependent on temperature, it is 10 h at 253 K and 10 min at 293 K. We have followed that evolution of phases with x rays at various temperatures. At 290 K, we observed the dimer phase of KC_{60} to transform into fcc (cubic lattice parameter a=13.97 Å) which subsequently transformed to the ortho-I polymer. This implies that the transformation occurs through the sequence: dimer→fcc→polymer. In RbC_{60} the fcc phase is not observed, only coexisting dimer and polymer. Nevertheless, we believe that the transformation of RbC_{60} goes through the same intermediate fcc phase but the fcc→polymer transformation runs much faster than the dimer→fcc.

The main experimental results are the occurrence of dimers with an interfullerene separation of 9.34 Å, and a rising susceptibility and electrical conductivity above 220 K, well below any structural phase transition. One hopes to be able to make a consistent interpretation of the physical properties of a material such as this quenched dimer phase of AC_{60} in terms of its structure. In the present case we are thwarted by the inability of the x-ray measurements to discern atomic structure at the level of, say, the covalently bonded chains in polymeric AC_{60}. We nevertheless take this opportunity to consider what models of dimer structure are compatible with our experimental data.

First, we note that there is every reason to believe that the dimers are covalently bonded. The observed interfullerene distance 9.34 Å is slightly larger than that in the conducting polymer phase (9.13 Å). However, it is much smaller than the 9.95 Å minimum observed van der Waals C_{60}-C_{60} distance. At the same time, we reject the possibility that the dimerization, the loss of electrical conductivity and spin susceptibility at low temperature is a Peierls transition. Peierls transitions occur in low dimensional metals where there is a small energy gain from opening a gap at the Fermi level. The possibly metallic fcc phase is three dimensional and the Fermi surface is not nested and thus no Peierls transition is expected. In quenched A_3C_{60}, the distortion is huge in contrast to systems in which the Peierls transition has been observed.

In view of the strong distortion in the dimer phase the gap in the conductivity is rather small, on the order of $2\Delta=0.2$ to 0.3 eV. The conductivity is not limited however to interdimer hopping along the dimer chains. The dimerized compound is not one dimensional since the nearest neighbor interfullerene distances are similar in all directions and are comparable to that of A_3C_{60} which is a good conductor.

The structural study shows that the C_{60} molecules form dimers but the question of the structure of the dimer itself remains open. Figure 5 shows three possible $(C_{60})_2^{2-}$ dimers. Consider first configurations such as Fig. 5(a) in which the $(C_{60})_2^{2-}$ is connected by one bond. Simple chemical considerations show that this dimer is diamagnetic. Therefore, a static structure based on this dimer cannot explain our susceptibility data above 220 K. Note that configurations such as Figs. 5(b) or 5(c) in which two interfullerene bonds occur may be paramagnetic or diamagnetic depending on the interactions between the spins on each of the constituent C_{60} molecules. For sufficiently small interaction between spins the dimer may have a diamagnetic ground state but may become paramagnetic at relatively low temperatures. This may explain the rise in susceptibility above 220 K.

Figure 5(b) shows the dimer version of the previously described polymer, consisting of a [2+2] cycloaddition across two double bonds. It is rather unlikely that this is the structure of the dimer. If it were, one would expect that the dimer could polymerize directly into the ortho-I phase. We have seen above that the dimer→polymer transformation occurs through an intermediate fcc phase. Indeed, we have seen that the dimers are unstable to decomposition into monomers at 290 K, whereas the polymer phase is stable up to 400 K. We are left with the interesting possibility that dimers with different configurations such as Figs. 5(b) and 5(c) may be formed depending on the thermal history. It is hoped that this work will motivate further quantum-chemical investigations of the stability of various C_{60} dimers.

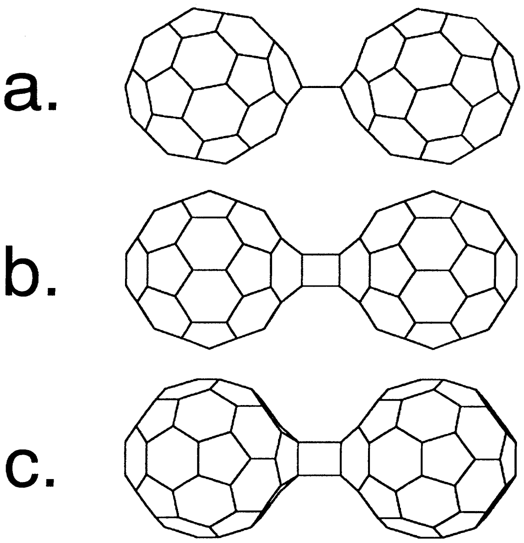

FIG. 5. Three possible configurations of the bonded $(C_{60})_2$ dimer. (a) represents the singly bonded dimer, (b) the dimer version of the ortho-I polymer, and (c) is another possible dimer in which bonding involves two carbon pairs of two pentagon-hexagon edges facing each other.

In conclusion the magnetic susceptibility, electric conductivity of quenched KC_{60} and RbC_{60} show a diamagnetic insulating ground state with a gap of approximately 0.3 eV. This is expected from the dimer structure in which C_{60} ions are covalently bonded into dimers. However, the full structure of the dimer remains an open question.

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