Quasi-One-Dimensional Electronic Structure in Orthorhombic RbC_{60}

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X-ray diffraction studies show that the stable phase of the alkali fullerene RbC_{60} is orthorhombic (o-RbC_{60}) below 350 K. C_{60} molecules form chains along **a** with an unusually short spacing of 9.12 Å and magnetic properties suggest that o-RbC_{60} is a quasi-1D metal with a transition to a spin density wave ground state at 50 K. The high temperature fcc phase of RbC_{60} may be stabilized below 300 K by quenching from 500 K; it is paramagnetic above 300 K and transforms into a nonmagnetic ground state between 300 and 250 K.

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Part of the interest in AC_{60} alkali fullerides discovered recently [1,2] lies in their unusual physical properties related to the low density of valence electrons. A comparison of AC_{60} and A_3C_{60} may be helpful in deciding questions like how important are intramolecular correlations for the occurrence of superconductivity [3]. At high temperatures these compounds have similar face centered cubic (fcc) structures with only the octahedral sites occupied [2] by alkaline ions in AC_{60} and both octahedral and tetrahedral sites occupied [4] in A_3C_{60}. The enhanced Pauli-like spin susceptibility of A_3C_{60} compounds [5,6] indicates a Fermi liquid behavior with important electron correlations. In AC_{60} compounds Coulomb correlations are expected to be even more important. The Mott-Hubbard insulating ground state suggested by Lof *et al.* [7] may be a reality in AC_{60} alkali fullerides. Indeed, in the high-temperature fcc phase CsC_{60} and RbC_{60} are not simple metals despite having a single electron per primitive cell. This is well demonstrated by the NMR Knight shift [8], which gives a Curie-like spin susceptibility corresponding to strong localization of unpaired electrons on the C_{60} molecules. Several authors have shown that the AC_{60} compounds undergo first order structural phase transitions [2,8–10] at about 350 K. However, the low-temperature structure and physical properties remain controversial.

In this Letter we show that below 350 K the stable phase of RbC_{60} is orthorhombic. The C_{60} molecules form chains along the crystallographic **a** direction with an unusually short intermolecular separation. The structure and electron spin resonance (ESR) data suggest that the system is a quasi-one-dimensional metal above 50 K. We propose that the one-dimensional electronic structure is unstable against a spin density wave state below 50 K where the spin susceptibility disappears.

The magnetic properties of fcc RbC_{60} are also interesting. In agreement with an earlier suggestion [10], the present x-ray diffraction data show that the high temperature fcc phase can be preserved as a metastable phase below 300 K by rapid cooling from 500 K and can be studied over a broad temperature range. Above 350 K we find that the spin susceptibility is close to that expected for a free paramagnetic spin with $S=\frac{1}{2}$ per C_{60} ion. The large spin susceptibility disappears between 300 and 250 K [10].

RbC_{60} was prepared by solid state reaction of a stoichiometric mixture of high purity (>99.9%) C_{60} powder and Rb metal in a sealed quartz capillary at 260 °C for 80 days. The specially shaped sample holder allowed x-ray diffraction and ESR measurements to be made on the same sample. X-ray powder diffraction spectra were recorded at beam line X3B1 of the National Synchrotron Light Source with a wavelength of 1.1500(3) Å. Spin susceptibilities were obtained by integration of 9 GHz ESR spectra.

At 465 K the x-ray diffraction spectrum [Fig. 1(a)] shows that the majority of the sample consists of fcc RbC_{60}, with less than 10% each C_{60} and Rb_3C_{60} present. The lattice parameter of 14.072(5) Å is in agreement with that reported by Zhu *et al.* [2]. As discussed below, this phase is not stable under 360 K. However, by rapidly cooling through the temperature range of 360 to 270 K the high temperature fcc phase may be quenched into a metastable state. As shown in Figs. 1(a) and 1(b), the only change observed between the 465 K spectrum and the 269 K quenched sample spectrum is a shift of the lines to higher angles due to the thermal contraction of the lattice. The lattice parameter of metastable fcc RbC_{60} is 13.975(5) Å at 269 K.

By slowly cooling from 465 K to ambient temperatures, the x-ray pattern of fcc RbC_{60} disappears and a new set of lines emerges [Fig. 1(c)]. This first order structural

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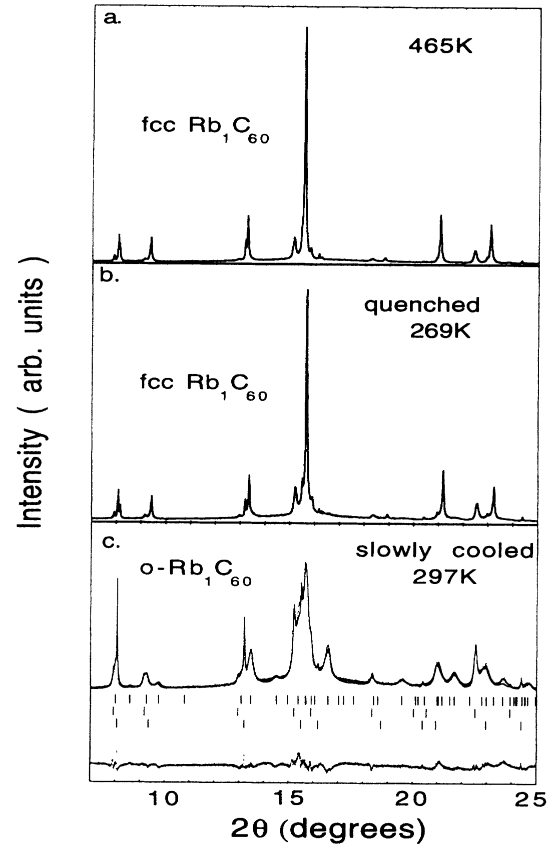

FIG. 1. X-ray diffraction spectra of RbC_{60}. (a) The fcc phase, stable above 350 K. (b) Metastable fcc phase, stabilized below 270 K by rapid cooling. (c) Orthorhombic phase, formed by slowly cooling through the structural phase transition at 350 K with minority phases of pure C_{60} (7%) and Rb_3C_{60} (8%). The calculated (solid line) and difference plots of the multiphase Rietveld refinement are also given. Ticks are the calculated reflection positions of the orthorhombic RbC_{60}, fcc Rb_3C_{60}, and fcc C_{60} phase.

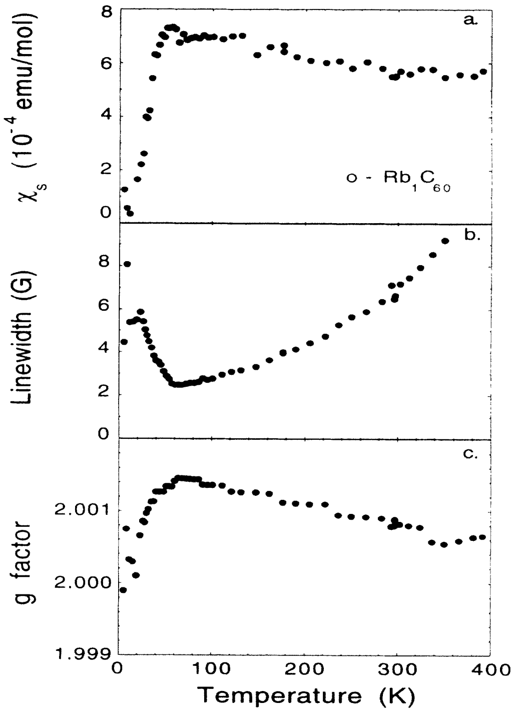

FIG. 2. Magnetic properties of o-RbC_{60}. (a) Above 50 K the spin susceptibility χ_s is large and approximately Pauli-like; the transition below 50 K is suggested to be a Peierls transition towards a spin density wave state. (b) The ESR linewidth is narrow despite the structural disorder as expected for a 1D conductor. The broadening and g shift (c) below 60 K is characteristic of a magnetic transition.

phase transition is hysteretic; the onset temperature on slow warming is 360 K. The composition does not change significantly during the transition since the same small amounts of pure C_{60} and Rb_3C_{60} are observed at all temperatures. Below 350 K the stable phase of RbC_{60} is orthorhombic (o-RbC_{60}) with lattice parameters $a=9.12$, $b=10.10$, and $c=14.26$ Å. The observed reflections obey the condition $h+k+l$ even, suggesting that the orthorhombic lattice is body centered. The high-temperature fcc phase may be viewed as a body centered tetragonal lattice with dimensions $a=b=9.95$ Å, $c=14.072$ Å, giving a simple picture of the low-temperature distortion. Note that the diffraction peaks are significantly broader, indicating that the orthorhombic distortion has broken and/or strained the cubic grains significantly.

There are several possible choices for the space group, and the detailed analysis of the structure will be presented in a future publication. Figure 1(c) shows a Rietveld fit of the x-ray diffraction pattern in the pseudo-body-centered space group *Pnnm*. The profile R factor for this fit is 7%. In this model, the contact between nearest neighbor fullerenes is by staggered pentagons, leading to an interfullerene carbon-carbon distance of 2.61 Å. The intensity is not sensitive to the orientation of fullerenes in this range of diffraction angles, but other orientations appear to lead unphysically small carbon-carbon distances. The broad ^{13}C NMR observed [8] at 298 K indicates that the molecules do not rotate.

We propose that o-RbC_{60} is a quasi-one-dimensional (quasi-1D) electronic conductor. The intermolecular C_{60} separation along **a** is unusually short while the separations along **b** and [111] are typical for both fulleride insulators and metals. Overlap of electrons in the intermolecular region along **a** is responsible for the shortness of the lattice parameter. The quasi-1D metallic character is supported by the ESR results of Fig. 2. The spin susceptibility of o-RbC_{60} is only slightly temperature dependent between 50 and 400 K [Fig. 2(a)]. The spin lattice relaxation rate T_1^{-1} (which in metals is measured by the electron spin resonance linewidth) is surprisingly narrow [Fig. 2(b)]. In 3D metals T_1^{-1} arises from the Elliott mechanism [11] and is proportional to the momentum scattering rate usually estimated from the resistivity. The broad x-ray lines indicate a large disorder which would give rise to a large T_1^{-1} in a 3D metal—especially in the presence of the heavy Rb ions. For example T_1^{-1} of the conduction electrons is 2 orders of magnitude larger [10] in the normal state of Rb_3C_{60} than in RbC_{60}. We ascribe this to a specific property of quasi-1D metals [12]. The matrix element for spin flip scattering vanishes for the Elliott mechanism and thus in quasi-1D metals the spin relaxation remains weak [2] even if disorder is important.

A phase transition is observed in o-RbC_{60} at 50 K. The spin susceptibility measured by ESR decreases by an order of magnitude, the ESR linewidth increases, and the g factor decreases rapidly between 50 and 10 K [Figs. 2(a)-2(c)]. (Below 10 K a small amount of paramagnetic impurities increases the susceptibility slightly.) A likely cause for this transition is an instability of the quasi-1D metal against the formation of spin density or charge density waves. The originally sixfold degenerate t_{1u} lowest unoccupied molecular orbital of the free C_{60} molecules splits into three twofold degenerate orbitals in the crystal field of the orthorhombic structure. The lowest level will be half filled in o-RbC_{60} and the charge density wave state corresponds to a doubling of the unit cell by an alternation of longer and shorter C_{60} intermolecular separations along the chains. If a spin density wave is formed the magnetic order doubles the unit cell along **a**. In both cases a gap opens at the Fermi level and the density of states measured by spin susceptibility vanishes at low temperatures. Although for spin density waves the static spin susceptibility perpendicular to the chains does not vanish, the conditions for the corresponding antiferromagnetic resonance are very different from those of the ESR. The temperature dependence of the linewidth and g factor is characteristic of antiferromagnetic correlations and thus supports a transition towards a spin density wave ground state. In $(TMTSF)_2PF_6$, a quasi-1D metal with a spin density wave ground state, the temperature dependence of the ESR spectrum [13] below the Peierls transition is similar to that observed in o-RbC_{60}. The idea of a transition to a spin density wave state is further supported by the observation [8] of an enhanced ^{13}C NMR spin lattice relaxation rate in the metallic phase of o-RbC_{60}. As pointed out by Tycko *et al.* [8], this may be due to antiferromagnetic fluctuations. In a quasi-1D system fluctuations may persist to temperatures well above the Peierls transition at which a 3D order develops.

The magnetic properties of the fcc RbC_{60} phase are also remarkable. Between 500 and 300 K the spin susceptibility increases with decreasing temperature (Fig. 3). This is in agreement with the ^{87}Rb NMR Knight shift [8] which showed a Curie behavior between 350 and 480 K. The spin susceptibility at 500 K corresponds to a paramagnetic system with a magnetic moment per C_{60} molecule corresponding to 0.7 ± 0.1 free $S = \frac{1}{2}$ spins. Thus although electrons are strongly localized, the spin susceptibility is somewhat reduced compared to a free system. Below 300 K the large susceptibility vanishes rapidly. No hysteresis in the susceptibility is observed below 270 K. (At higher temperatures the fcc metastable phase transforms into the stable o-RbC_{60} phase.) Magnetic ordering between 300 and 250 K as the reason for the decrease of spin susceptibility is not supported by the ESR data which show a narrowing of the line and an increase of the g factor with decreasing temperature. A relatively large Curie susceptibility corresponding to 1% of C_{60}^- paramagnetic defect ions is observed at low temperatures. These ions are not observed in the slowly cooled sample and are thus defects of the fcc RbC_{60} phase. Contrary to expectations for a magnetically ordered system in which internal fields would broaden the resonance, the ESR line of the paramagnetic defects is very narrow (2-3 G).

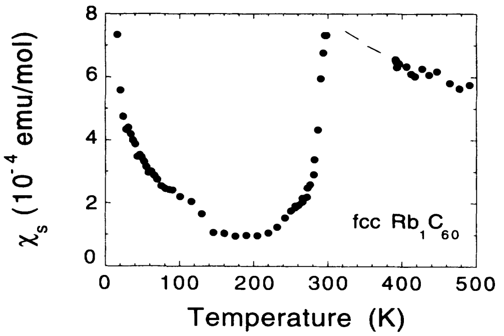

FIG. 3. Magnetic spin susceptibility of fcc RbC_{60}. Above 400 K in the stable state; below 300 K in the metastable state. χ_s at 500 K corresponds to a paramagnetic state with 0.7 ± 0.1 spins per C_{60} molecule. The transition below 300 K is probably to a nonmagnetic state. Data between 15 and 300 K are taken with increasing temperature after an initial rapid quench from 500 K.

The difference in the electronic structures of the orthorombic and fcc phases is surprisingly large. At the 400 K structural phase transition the spin susceptibility changes by only 10% while the ^{87}Rb NMR shift changes by a large factor [8] showing that the overlap of conduction electrons with alkaline ions changes dramatically.

In conclusion, the 1D and 3D character of the electronic structure is the underlying reason for the dramatically different magnetic properties of orthorhombic and face centered cubic RbC_{60}. In both cases a simple uncorrelated band picture would predict a metallic behavior. We suggest that the quasi-1D electronic structure of o-RbC_{60} leads to a spin or charge density wave ground state. In fcc RbC_{60} electron-electron correlations localize electrons on the C_{60} molecules and at high temperatures a large Curie-like susceptibility is observed. Below 300 K the paramagnetic state transforms into a state with vanishingly small spin susceptibility and ESR data suggest that the ground state of fcc RbC_{60} is nonmagnetic.

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