



Structure and properties of the stable two-dimensional conducting polymer Mg_5C_{60}

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We present a study on the structural, spectroscopic, conducting, and magnetic properties of Mg_5C_{60} , which is a two-dimensional (2D) fulleride polymer. The polymer phase is stable up to the exceptionally high temperature of 823 K. The infrared and Raman studies suggest the formation of single bonds between the fulleride ions and possibly Mg-C₆₀ covalent bonds. Mg_5C_{60} is a metal at ambient temperature, as shown by electron spin resonance and microwave conductivity measurements. The smooth transition from a metallic to a paramagnetic insulator state below 200 K is attributed to Anderson localization driven by structural disorder.

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I. INTRODUCTION

The unusual physical and structural properties of alkali metal intercalated fulleride polymers have received considerable attention since the discovery in 1994 of the linear AC_{60} ($A=\text{K}, \text{Rb}, \text{Cs}$) conducting polymers.¹ Chemical reactions between charged fulleride ions in solids are rather common. The polymer phases usually form spontaneously or under a mild pressure from the monomeric crystalline salts. Polymers of C_{60}^{n-} anions are usually unstable above temperatures of about 400 K. The depolymerization is reversible, in contrast to photopolymerization² and pressure polymerization of neutral C_{60} .^{3,4} According to quantum chemical calculations,⁵ [2+2] cycloaddition is favored in $A_n\text{C}_{60}$ for low values of n , and configurations with single interfullerene bonds are more stable for $n \geq 3$. In agreement with these expectations, the stable form of AC_{60}^- is a cycloaddition polymer,⁶ while single intermolecular bonds occur between C_{60}^{n-} anions in Na_4C_{60} (Ref. 7) and $\text{Na}_2\text{RbC}_{60}$.⁸ Single and double bonds can simultaneously appear, as has been recently demonstrated in Li_4C_{60} ,^{9,10} wherein single bonds connect polyfulleride chains held together by [2+2] cycloaddition bonds.

Fulleride polymers have small electronic bandwidths and large on-site electron repulsion and are thus strongly thus correlated electron systems. Small differences in the lattice parameters and/or variations in the chain orientation¹¹ can profoundly change the ground state. For example, the linear polymer KC_{60} has a metallic ground state while RbC_{60} and CsC_{60} with the same type of polymer chains but different chain orientations undergo a metal-insulator transition to an antiferromagnetic spin density wave ground state.¹² Electron-electron correlations play an important role in two-dimensional (2D) fulleride polymers as well: Na_4C_{60} is a strongly correlated metal,⁷ while Li_4C_{60} is a nonmagnetic insulator.¹⁰

In this paper, we present a study of the structure and physical properties of the recently synthesized fulleride polymer Mg_5C_{60} . In a previous study of Mg_xC_{60} , a stoichiometric compound¹³ was reported for $x=4$. In the present work, we

improved the synthesis and conclude from a series of samples with varying Mg content that the homogeneous phase lies in a range of Mg concentrations between $x=5$ and $x=5.5$. Mg_5C_{60} is the only known example of an alkaline earth fulleride polymer. The polymer phase was found to be stable up to the remarkably high temperature of 823 K by electron spin resonance. Other fullerene polymers are stable to much lower temperatures and depolymerize at about 400–500 K. We find that Mg_5C_{60} is a 2D polymer that is metallic at a high temperature and undergoes a gradual transition to an insulating ground state as the temperature is lowered.

Previous studies of alkaline earth fullerides mostly focused on Ca_xC_{60} and Ba_xC_{60} (Refs. 14 and 15) superconductors, which are not polymers. An early study of Mg doped fulleride films reported an insulating behavior for all Mg concentrations,¹⁶ which is in disagreement with our present results.

II. EXPERIMENT

Samples of Mg_xC_{60} with nominal concentrations $x=4-6$, which are in steps of $\Delta x=0.5 \pm 0.05$, were prepared by solid state reaction between C_{60} and pure Mg powder under argon atmosphere in a dry box. The powder mixture was placed in carbon steel containers to avoid reaction between the Mg grains and quartz vessels. Mg grain surface activation at 753 K was followed by several annealing steps at temperatures from 653 to 723 K. To improve the homogeneity of the sample, we used Mg powder with smaller grain sizes than in the previous preparation.¹³ Powders were reground before each annealing step.

X-ray powder diffraction was performed using a HUBER G670 Guinier image plate camera in transmission mode and highly monochromatic $\text{Cu } K\alpha_1$ radiation. Infrared transmission spectra were recorded on pressed KBr pellets with a Bruker IFS 28 Fourier transform infrared spectrometer under dynamic vacuum. Raman spectra were collected using a T64000 Jobin-Yvon spectrometer in triple grating configura-

tion with spectral resolution better than 3 cm^{-1} . The 532 nm line of a frequency-doubled neodymium doped yttrium aluminum garnet laser, Nd-YAG, was the excitation source. The diameter of the spot was $100\ \mu\text{m}$ corresponding to a nominal irradiance of about 150 W/cm^2 .

Microwave conductivity was measured at 10 GHz on fine Mg_5C_{60} powders mixed with high purity SnO_2 powder to electrically isolate the grains. A 10 GHz copper cylindrical TE011 resonant cavity was used for the cavity perturbation technique conductance measurements.^{17,18} In this method, changes in the quality factor are measured using lock-in detection of the frequency modulated response. The sample is placed at the cavity center where the microwave magnetic field is maximum and microwave currents encircle the grains. This geometry is well adapted for fine powders because the microwave electric field is not shielded by depolarization effects.¹⁸ The typical grain size was much smaller than the microwave penetration depth, as confirmed by the symmetric Lorentzian electron spin resonance (ESR) line shape measured at the same frequency. The temperature dependence of the conductivity $\sigma(T)$, is proportional to $1/Q - 1/Q_0$. Q and Q_0 , which are the quality factors of the cavity with and without the sample, respectively, were measured in two separate runs. Q_0 was about 16 000 and it changed little with temperature. Ohmic losses of a single spherical grain with radius r and conductivity σ are proportional to $r^5\sigma$. The determination of the absolute value of the conductivity is not possible without a detailed knowledge of the distribution of r .

ESR spectroscopy was performed at 9 and 225 GHz on samples sealed in quartz tubes under 200 mbar He pressure. At 9 GHz, a commercial Bruker ELEXSYS 500 spectrometer was used, the 225 GHz spectra were recorded by a homebuilt spectrometer. The spin susceptibility was obtained by integrating the ESR spectra. MgO doped with 1.5 ppm of Mn^{2+} ions was the ESR intensity reference to obtain the susceptibility between 100 and 300 K. Below 100 K, the Mn:MgO ESR saturates and fine orthorhombic polymeric KC_{60} powder (a low conductivity metal with a temperature independent susceptibility) was used as an intensity reference.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Powder diffractograms of a series of Mg_xC_{60} salts (Fig. 1) show that the samples are single phase for nominal concentration values between 5 and 5.5. The peak at about 36.3° demonstrates that above a nominal composition of $x=5.5$, some Mg metal is present. The x-ray results also indicate that Mg_5C_{60} is not a line phase, the structure presented here and in Ref. 13 comprises a range of stoichiometries between $x=5$ and 5.5. In the previous paper, the single phase material has been obtained for a nominal composition of $x=4$ and has been indexed as rhombohedral with lattice parameters $a=b=9.22\ \text{\AA}$, $c=25.25\ \text{\AA}$, $\gamma=120^\circ$. These values indicate the formation of two-dimensional hexagonal C_{60} polymeric sheets in the ab plane. The material belongs to the $R\bar{3}m$

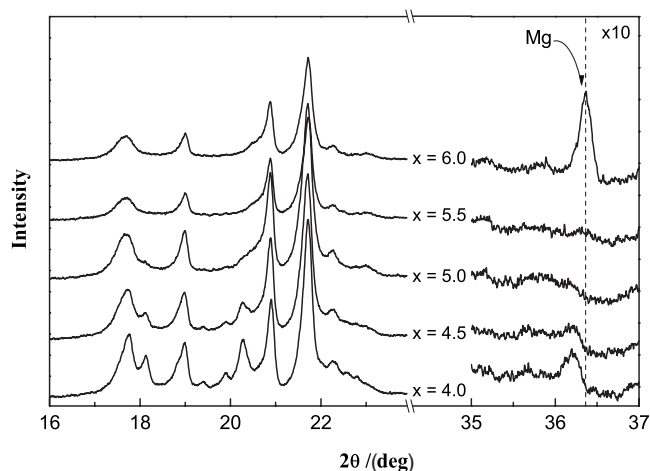


FIG. 1. X-ray powder diffraction data for a series of Mg_xC_{60} polymers, with nominal concentrations x varying from 4.0 to 6.0. The material is single phase for $x=5$ and 5.5. The dotted line above 36° corresponds to Mg metal.

space group. C_{60} molecules are positioned at the fractional coordinates $(0,0,0)$, $(2/3,1/3,1/3)$, and $(1/3,2/3,2/3)$, while the Mg positions are $(0,0,0.23)$ and $(0,0,0.43)$. The improved synthesis method using fine-powdered magnesium metal resulted in a more reliable magnesium content than the previous one. However, even in the better defined material, we can determine the positions of only four of the five magnesium ions. A range of alkali concentrations without any change in the structure of the polymer has been observed in Li_xC_{60} ($3 \leq x \leq 5$),¹⁰ with the structural parameters given by a Rietveld fit corresponding to $x=4$. Subsequent photoemission data on Li_xC_{60} thin films with the same structure showed an incomplete charge transfer, which do not change throughout the homogeneity range.¹⁹

B. Infrared and Raman spectroscopy

The infrared transmission and Raman scattering spectra of Mg_5C_{60} are shown in Fig. 2. The low-frequency part corre-

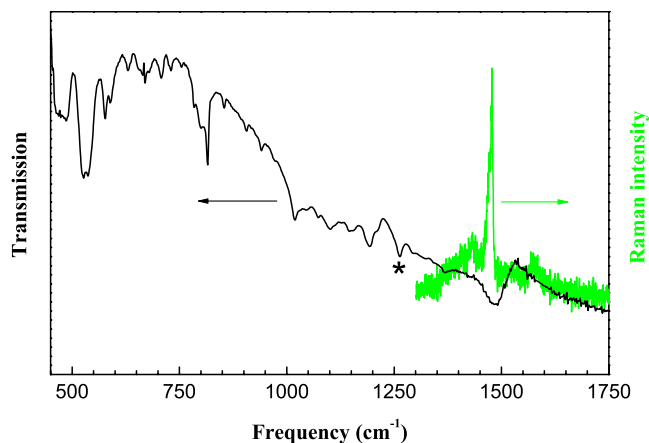


FIG. 2. (Color online) Infrared transmission and Raman scattering spectra of Mg_5C_{60} . The feature at 1480 cm^{-1} , which is visible in both spectra, is assigned to the $A_g(2)$ vibrational mode of C_{60} . The infrared line marked with an asterisk is an extrinsic impurity mode.

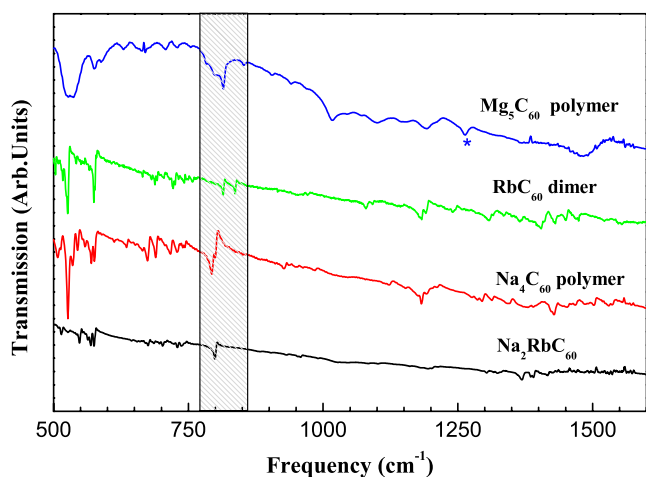


FIG. 3. (Color online) Comparison of the infrared spectra of various singly bonded fulleride oligo- and polymers. All the spectra show an absorption line around 815 cm^{-1} (indicated by the bar), which is attributed to single bonds between C_{60} molecules. The infrared line marked with an asterisk is an extrinsic impurity mode. The curves are shifted along the vertical axis for clarity.

sponds to a symmetry-reduced C_{60} molecule with the principal T_{1u} modes at 523 , 576 , and 1193 cm^{-1} and several new modes, especially in the region between 700 and 900 cm^{-1} . Such marked changes in the spectrum indicate a symmetry lowering to an extent that is usually caused by intermolecular bonds (i.e., polymerization)²² and not just deformation of isolated C_{60} balls in a crystal. The line around 815 cm^{-1} is of particular interest. This line appears in the spectrum of all C_{60} -based polymers,^{20,21} wherein the C_{60} molecules are connected by single bonds (see Fig. 3). We consider the appearance of this characteristic peak in Mg_5C_{60} as proof for single bonds between fulleride ions.

The high-frequency region around the $T_{1u}(4)$ mode shows an unusual pattern, which is dominated by a broad feature around 1480 cm^{-1} . This feature cannot be explained by a shift in the $T_{1u}(4)$ mode by charge transfer from the Mg atom nor by polymerization effects, which are both known to reduce the vibrational frequencies.^{22,23} Instead, we assign this peak to the $A_g(2)$ vibrational mode, which is Raman active in undistorted C_{60} . Our assignment is supported by the fact that the peak is also dominant in the Raman spectrum. A similar effect was reported for C_{60} monolayers adsorbed on metal²⁴ and semiconductor surfaces.²⁵ In those systems, an intense infrared absorption above the highest-frequency T_{1u} mode is observed, together with a Raman counterpart,²⁶ which is attributed to the $A_g(2)$ mode rendered infrared active by symmetry reduction and amplified by the “vibrational phase relaxation” mechanism.²⁷ Prerequisites for this mechanism are (1) a free-electron continuum and (2) low-frequency vibrational or translational modes, which mediate the coupling. According to our ESR and microwave data (see below), conducting electrons are present in Mg_5C_{60} and it is known from Raman spectroscopy of C_{60} photopolymers that intermolecular vibrations appear around 100 cm^{-1} (Ref. 2), thus, both criteria are met. In the case of Mg_5C_{60} shown in Fig. 2, the mode is both infrared and Raman active but, unlike in Refs. 24 and 25, in both cases shifted up by 12 cm^{-1} compared to

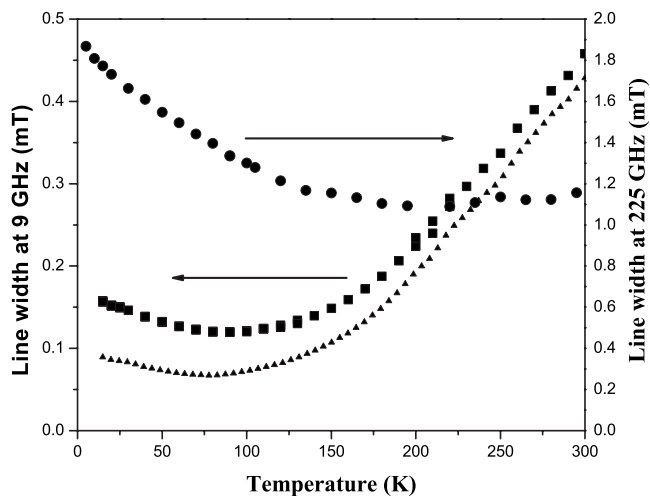


FIG. 4. Temperature dependence of the ESR linewidth of Mg_5C_{60} at 9 GHz (squares) and 225 GHz (circles). The temperature dependence of the frequency independent component of the linewidth $a(T)$ is also reported (triangles). For temperatures above 175 K, the linewidth at 9 GHz linearly increases with temperature, as is expected in metals in which the main relaxation mechanism is the electron-phonon interaction.

the 1468 cm^{-1} pristine $A_g(2)$ mode. Such blueshift, although smaller, has been observed in C_{60} monolayers adsorbed on platinum,²⁸ wherein it was explained by covalent bonding to the metal, resulting in electron back transfer from the fullerene to the metal surface. Covalent bonding to at least some of the Mg ions cannot be excluded in the present case either considering the close values of the Mg ionization potential and the lowest unoccupied molecular orbital level of C_{60} . The phenomenon described here warrants further investigation since it was not seen in bulk fulleride salts before.

C. Microwave conductivity and electron spin resonance

In the following, we discuss the microwave conductivity and ESR measurements, which show that Mg_5C_{60} is metallic above room temperature and becomes insulating at low temperatures.

The ESR spectrum consists of a single Lorentzian line at all temperatures both at 9 and 225 GHz, confirming the phase purity of the sample. Phase inhomogeneities usually split the line or at least inhomogeneously broaden it due to differences in the g factor. If the Mg concentration were inhomogeneous, then the high-frequency ESR lines would be distorted especially in the low temperature insulating state where spatial variations are not averaged by spin diffusion.

In Fig. 4, we show the temperature dependence of the ESR linewidth. The 9 GHz line is a symmetric Lorentzian with a 0.45 mT linewidth at room temperature. The line broadens with increasing frequency. The frequency and the temperature dependences of the linewidth may be separated to give $\Delta H = a(T) + b(T)H$. The frequency independent term, $a(T)$, is almost constant below 100 K (see Fig. 4) and linearly increases with temperature as in metals, in which the main relaxation mechanism is the electron-phonon interaction.³¹ The term $b(T)$ increases with frequency and

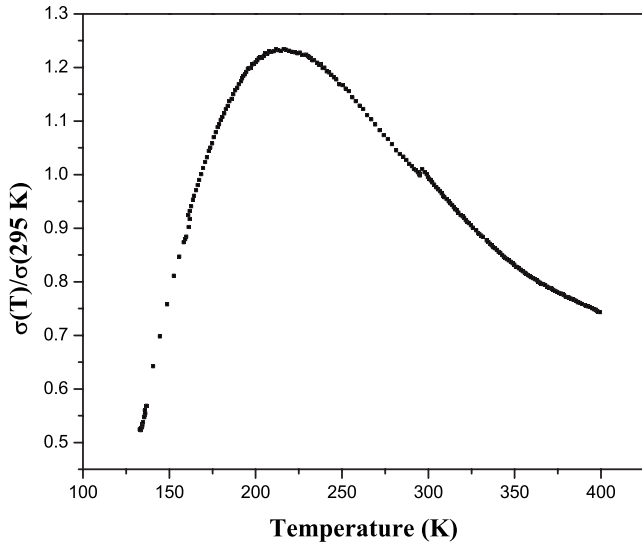


FIG. 5. Microwave conductivity at 10 GHz of Mg_5C_{60} . The conductivity has a smooth transition from a metal to an insulator behavior at about 200 K, which we attribute to Anderson localization of the electronic states.

with lowering of the temperature. The line broadening at 225 GHz is due to a partially averaged g -factor anisotropy. We attribute the broadening at $T < 200$ K (see Fig. 4) to the inhomogeneous interaction between paramagnetic defects randomly distributed in the lattice.

Figure 5 displays the temperature dependence of the microwave conductivity of Mg_5C_{60} normalized to 295 K. At high temperatures, the conductivity decreases with increasing temperature, as is usual in metals wherein scattering is due to phonons. The low temperature behavior is different from that of usual metals. The conductivity has a broad maximum and decreases below 200 K. This behavior corresponds to a smooth transition between metallic and insulating states.

A deeper insight into the nature of this transition is given by the temperature dependence of the spin susceptibility shown in Fig. 6. For $T \geq 200$ K, the spin susceptibility has a value of 2×10^{-5} emu/mole and is almost independent of temperature, as expected for the Pauli susceptibility of a degenerate electron gas. In normal metals, the spin susceptibility is related to the density of states at the Fermi level $n(E_F)$: $\chi = 1/4 g^2 \mu_B^2 n(E_F)$, where g is the spectroscopic g factor and μ_B is the Bohr magneton. At lower temperatures, a Curie contribution characteristic of a small concentration of localized spins dominates the ESR spectrum. The change of the temperature dependence of the static susceptibility from Pauli to Curie-like is gradual and there is no well-defined phase transition. The presence of a gap in the electron energy spectrum can be excluded because the spin susceptibility does not disappear even at the lowest temperatures. We do not observe a Mott–Hubbard transition, which usually has a well-defined transition temperature and gives rise to a magnetically ordered ground state. We suggest instead that this smooth transition to an insulating ground state is due to Anderson localization. At a certain degree of disorder of the lattice, the electronic wave functions with an energy below

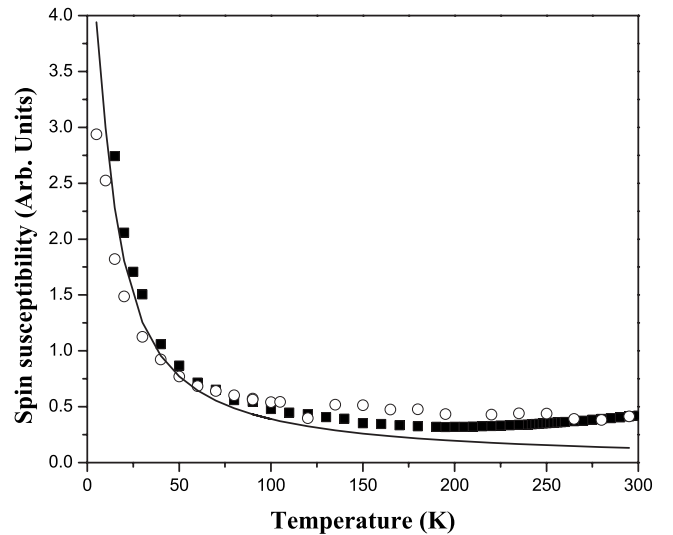


FIG. 6. Temperature dependence of the spin susceptibility of Mg_5C_{60} . 225 GHz ESR measurements (empty circles) are normalized to the 9 GHz ones (squares) at 300 K. The continuous line is the Brillouin function of spin 1/2 in 8.1 T field normalized at 50 K to the 225 GHz ESR measurement. At all the frequencies, the spin susceptibility shows a broad transition from a Pauli- to a Brillouin-like temperature dependence, suggesting a localization of the electronic states. The susceptibility does not disappear at the lowest temperatures, excluding a gap in the excitation spectrum.

the mobility edge, E_c , become localized.^{29,30} If the Fermi energy lies below E_c , the ground state is insulating. On the other hand, electrons become delocalized and the behavior is metallic when the temperature is much higher than E_c/k_B . The temperature dependence of the conductivity of Mg_5C_{60} is dominated by the thermal activation of the electrons above the mobility edge at low temperatures and by the electron-phonon relaxation for $T > 200$ K. The description of the behavior near 200 K, where the two contributions are comparable, requires a deeper knowledge of the disorder potential and of the phonon structure.

We measured a lower limit of the depolymerization temperature by searching for changes in the ESR spectra after annealing at higher temperatures. The sealed Mg_5C_{60} sample was heated at a rate of 10 K/min to each temperature, kept there for 15 min, and quenched into water and then the 9 GHz ESR spectra were recorded at ambient temperature. We repeated this cycle twice in 25 K steps between 300 and 848 K. We found that treatment up to 823 K, leaves the ESR spectrum unchanged. At 848 K, the ESR spectrum and the color of the quartz sample holder changed. These changes indicate reaction of Mg (diffusing out of the sample) with quartz. It is not clear whether without this reaction depolymerization would take place. We conclude that the polymer phase is stable for at least 30 min at 823 K.

IV. CONCLUSION

Mg_xC_{60} with $x=5-5.5$ is a single phase, two-dimensional fulleride polymer. X-ray diffraction indicates a finite

stoichiometry range with the same structure. Vibrational spectroscopy reveals that the Mg-fullerene interaction is more complicated than a simple charge transfer with a possible covalent component. Microwave conductivity shows that Mg_5C_{60} is metallic for $T > 200$ K and this is confirmed by the temperature dependence of the spin susceptibility and of the ESR linewidth. We attribute the transition from metallic to paramagnetic insulating states below 200 K to a disorder driven Anderson localization. The stability of the polymeric structure of Mg_5C_{60} up to temperatures above 800 K is exceptional, all other polymers of charged fullerenes con-

nected by single or double C-C bonds decompose at much lower temperature.

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