



Probing structural phase transitions of crystalline C_{60} via resistivity measurements of metal film overlayers

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Abstract

The electrical resistance of thin silver films deposited on C_{60} crystals shows anomalies near 261, 240, and 100 K. These temperatures coincide, respectively, with the bulk rotational, surface rotational, and quenched disorder structural phase transitions of crystalline C_{60} . Films of other metals on C_{60} show similar behavior. Our findings demonstrate that thin metal film overlayers are sensitive probes of the structural phase transitions in C_{60} , and also provide evidence for a novel structural-electronic interaction at the metal/ C_{60} interface.

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1. Introduction

Electronic, magnetic, and structural phase transitions in crystalline solids continue to be among the most active research topics of solid state physics. Experimental techniques for studying structural phase transitions in bulk insulators include X-ray and neutron diffraction, X-ray fine structure absorption, differential scanning calorimetry, and nuclear magnetic resonance. Some of these techniques have been successfully applied to the fullerene C_{60} , which crystallizes into a van der Waals solid with rich structural properties.

At room temperature the C_{60} crystal is fcc with each C_{60} molecule in nearly free rotation. Upon cooling through 261 K the C_{60} molecules lose two rotational degrees of freedom and acquire strong orientational correlation with

their neighbors, ratcheting around one of the four $\langle 111 \rangle$ axes. This rotational ordering transition (ROT) is also a first order fcc to sc structural transition [1]. At a surface the effect of reduced symmetry lowers the corresponding transition to ~ 230 K [2]. Cooling below 261 K slows the ratcheting, stopping it entirely near 50 K in the bulk. However, because there are two nearly degenerate (~ 11.4 meV) orientations separated by a substantial (290 meV) potential barrier, the rotational ordering is incomplete even in the low temperature limit. Below 90 K the occupation of the nearly degenerate states does not change, so this temperature is identified with the quenched disorder transition [3].

In this paper, we present measurements of the electrical resistance of thin metal films deposited on crystalline C_{60} substrates, and show that such measurements are also sensitive probes of structural phase transitions of the underlying C_{60} . Resistive evidence for structural phase transitions in crystalline C_{60} has been noted before [4–6], but the effects have been small ($\leq 10\%$) and monotonic. In addition, we observe a large and transient resistance drop near 260 K, which provides evidence for an extraordinary

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structural-electronic coupling in the metal/ C_{60} system in the vicinity of the structural phase transition temperature.

2. Experiments and results

Our C_{60} crystals were grown by subliming powder from MER Corporation (99.5% purity) in a flowing Ar atmosphere. The crystals so produced were several millimeters in size and had flat surfaces. Metal films (Ag, Au, Cu, Pd, Pt) were dc-sputtered onto a crystal face to various thicknesses as determined by a 6 MHz quartz-crystal monitor. Generally, the deposition rate was controlled at 0.1 nm/s. Silver paint contacts on the metal films were used for four-probe quasi-dc electrical resistance measurements. A helium gas-flow probe provided cooling from room temperature down to ~ 16 K. Both cooling and warming gave consistent results, but only warming data will be presented because of its superior temperature resolution.

Fig. 1(a) shows a scanning electron microscope (SEM) image of a nominally 10 nm thick Ag film deposited on C_{60} . The film is not uniform, but is granular with an average feature size of ~ 10 nm and has a morphology reminiscent of thin film percolation networks. Electrical measurements at room temperature on this film indicate an average resistivity $\rho \sim 6 \mu\Omega$ cm, ignoring the film inhomogeneity.

As expected, this value significantly exceeds the resistivity $\rho \sim 1.6 \mu\Omega$ cm usually observed for high quality homogeneous Ag specimens.

Fig. 1(b) shows the temperature dependent resistance $R(T)$ of a 10 nm thick Ag film on C_{60} , similar to the one pictured in Fig. 1(a). Relative to the typical behavior of Ag films on benign substrates, several anomalies are present in Fig. 1(b). First, instead of displaying linear temperature dependence, there is a slope change near 100 K. Second, as the sample warms through 240 K, the resistance decreases, reaching a minimum value (0.17Ω) even smaller than the residual resistance ($\sim 0.18 \Omega$). Third, at 261 K the resistance shows a very sharp jump upward with increasing temperature. Fourth, for $T > 261$ K, although the $R(T)$ curve becomes linear again, its slope is not the same as that between 100 and 240 K. Control experiments with Ag films similarly deposited on mica or glass substrates do not show any of these anomalies. As we discuss later in this report, the three anomalies of Fig. 1(b) at $T = 100$, 240, and 260 K are associated with well-known structural phase transitions of the underlying C_{60} crystal.

The measurements described above have been repeated as a function of sample thermal history, for different Ag film thicknesses, and for films composed of different metals. Fig. 2(a) shows the $R(T)$ curves of one 10 nm Ag film over multiple thermal cycles (only warming curves are shown for

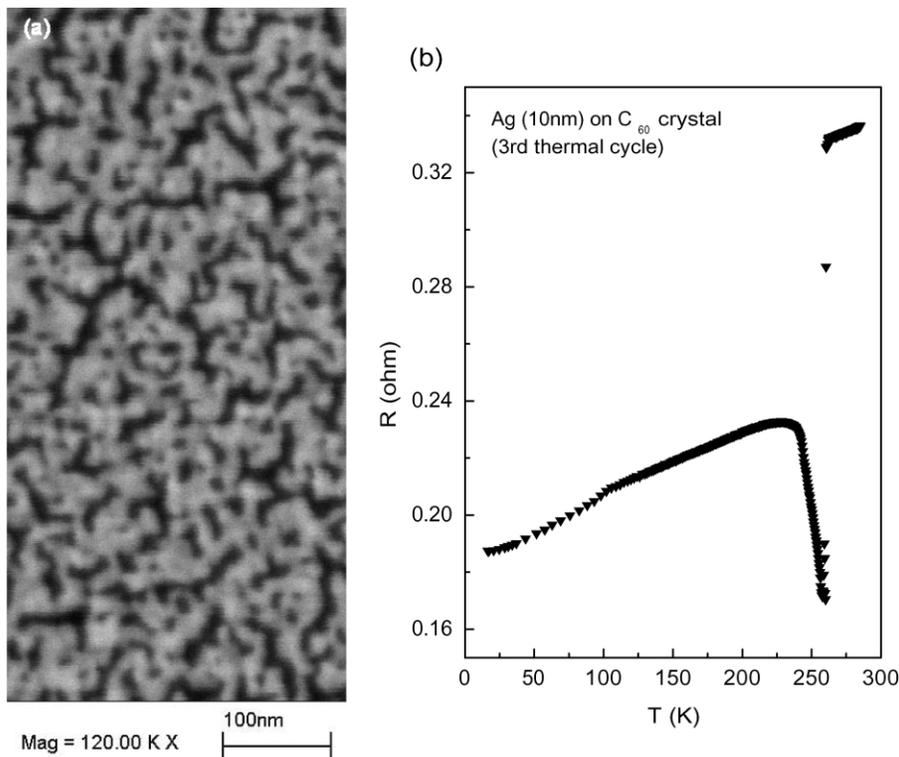


Fig. 1. (a) Scanning electron micrograph of a 10 nm silver film on a C_{60} crystal. Scale bar is 100 nm. (b) Resistance vs. temperature for a similar film.

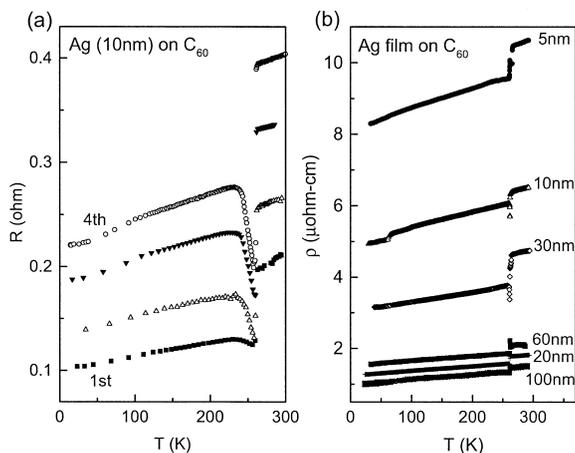


Fig. 2. (a) Resistance behavior of the 10 nm Ag film on C_{60} with thermal cycling. Only warming curves are shown for clarity. (b) Resistivity vs. temperature of Ag films with different thicknesses on C_{60} crystals (first thermal cycle).

clarity). The residual resistance increases monotonically with thermal cycling, and the anomalous behavior between 240 and 261 K becomes more dramatic. The resistance dip near 240 K is not pronounced at first, but becomes effectively deeper, finally reaching a minimum value even lower than the residual resistance. The resistance jump at 261 K also increases with thermal cycling, as well as the slope of $R(T)$ between 100 and 240 K. Similar behavior was observed in a different sample with a 5 nm thick Ag film.

Fig. 2(b) shows the effect on the resistivity of systematically varying the thickness (t) of the Ag films between 5 and 100 nm. All data sets in Fig. 2(b) are for different newly prepared samples, measured during their first thermal cycle (where the resistive anomalies are smallest). The three-dimensional resistivity ρ has been calculated using the measured resistance R , the in-plane film/contact geometry, and the nominal film thickness as determined by the sputtering system crystal monitor. No attempt has been made to correct for film granularity. With the exception of the 20 nm sample (which was prepared with a higher deposition rate that likely produced a less granular film), the resistivities $\rho(T)$ generally increase with reduced thickness. However, the slope $d\rho/dT$ between 100 and 240 K also increases notably with reduced thickness, in apparent violation of Matthiessen's rule. The thickest film has a room temperature resistivity of approximately $1.6 \mu\Omega \text{ cm}$, consistent with that expected for a uniform silver film in the bulk limit.

Fig. 3 shows the $R(T)$ data from the first thermal cycle of four thin metal films on C_{60} crystals, where the metals are Pd (20 nm), Cu, Pt, and Au (all 10 nm). Although the $R(T)$ curves differ markedly, the anomaly near 261 K generally reproduces for each metal. For Pd and Pt films, the resistance dips are more evident than those of Au and Cu films. The Pt $R(T)$ curve shows apparently semiconducting

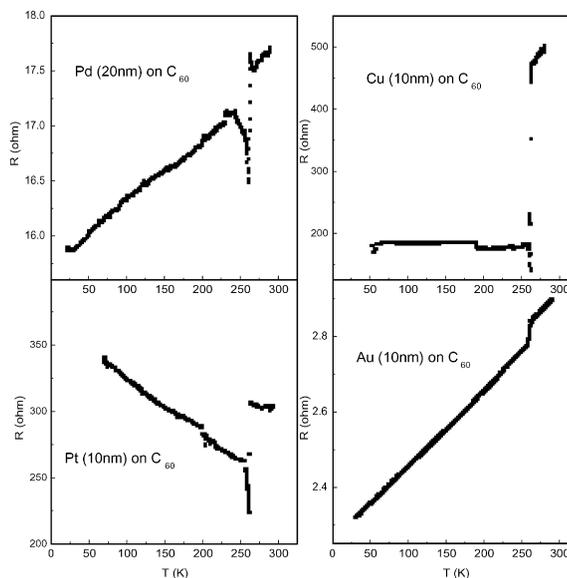


Fig. 3. Resistance vs. temperature behavior for Au, Cu, Pd, and Pt films on C_{60} crystals.

behavior, possibly due to disconnected granular structures with thermally activated conductivity. The overall results suggest that the anomalies are universal to different metallic films and a general mechanism must be considered for this metal- C_{60} interface effect.

3. Discussion

Crystalline C_{60} is a band insulator with room temperature resistivity in excess of $10^6 \Omega \text{ cm}$, while silver is a good electrical conductor with a resistivity of $1.6 \mu\Omega \text{ cm}$ at room temperature. Due to this 11 order of magnitude difference, one would naively expect that the resistance measurement on the Ag- C_{60} system would only reflect the behavior of pure Ag. However, the observed anomalies clearly coincide with the structural phase transitions of crystalline C_{60} . The slope change at 100 K is near the quenched disorder phase transition, and the anomalies at 240 and 261 K correspond to the surface and bulk rotational ordering transitions, respectively. The correlation between the resistance anomalies and the phase transitions suggests a strong coupling between the Ag film and the C_{60} crystal.

The clear relationship between the structural phase transitions of the C_{60} crystals and the resistivity anomalies in the metal films is the main result of this paper. To explain this relationship we propose a simple model where the thin metallic film acts as a resistive strain gauge, and thus is sensitive to the unusual phase structural phase transitions (including lattice discontinuities) of the substrate crystal. Although some features of the data are well accounted for by this model, others are not. The most serious failing of the model is an inability to account for, even qualitatively, the

sharp resistance dip near 260 K. To some extent this ‘failing’ highlights the most interesting feature of our data, for the unexplained resistance dip at C_{60} ’s ROT seems to indicate the presence of a truly novel interaction.

A key enabling feature of the strain gauge model is a differential thermal expansion $\Delta\alpha$ between the metallic overlayer and the substrate crystal. In the range 100–300 K but away from the 261 K transition the linear thermal expansion coefficients of Ag and C_{60} , though comparable, are not matched: $1.9 \times 10^{-5}/K$ vs. $2.1 \times 10^{-5}/K$, respectively. Below 100 K α for Ag decreases with decreasing temperature while for C_{60} α is relatively temperature independent [3,7]. At the ROT the lattice parameter of C_{60} changes abruptly by more than 0.3% [1]. Although the simplest geometric effect gives a contribution orders of magnitude too small [8] to explain our observations, granularity could enhance the film’s sensitivity to geometric changes. The network evident in Fig. 1(a) supports the granularity hypothesis. Thus, differential thermal expansion could be a factor in driving the $d\rho/dT$ anomalies that are observed over the entire measurement range and are especially dramatic at the lattice parameter discontinuity.

The strain gauge picture might also explain the results of our thermal cycling measurements. Fatigue created by mismatched thermal expansion coefficients is a problem well known in the semiconductor industry [9], and we observe qualitatively that repeated cycling often leads to macroscopic cracking of the sample. Viewing the film as a network of current paths in parallel, we hypothesize that thermal cycling creates microscopic fractures that break some paths. In the data of Fig. 2(a), for instance, the residual resistance ratio ($RRR \equiv R(300\text{ K})/R(T \rightarrow 0\text{ K})$) is a constant ~ 2 for the four curves. The assumption that thermal cycling cuts some current paths explains this observation (the resistance increases without changing the RRR), for eliminating resistors from a parallel network would produce exactly this behavior. If, on the contrary, thermal cycling were introducing defects, the RRR would be expected to decrease while the resistance increased.

Fig. 4 shows the data from Fig. 2(a) rescaled according to this hypothesis. Between the normalization points of 40 and 230 K the four curves overlap well, which confirms only that the data are reasonably linear in this temperature region. However, even above the 260 K discontinuity the same approximate scaling continues to hold. This result implies that the relative magnitude of the discontinuity is an intrinsic property of the film: the resistivity of the silver film reflects changes in the lattice parameter of the substrate crystal. (By hypothesis this resistivity cannot be calculated from the measured resistance, since the microscopic cracks caused by thermal cycling create substantial geometric uncertainty.) The slow climb of the resistance from 20 to 230 K, and the jump from 230 to 260 K, both reflect the corresponding thermal expansion of the substrate crystal.

Although the strain gauge picture provides a useful view of our observations, the model is incomplete and probably

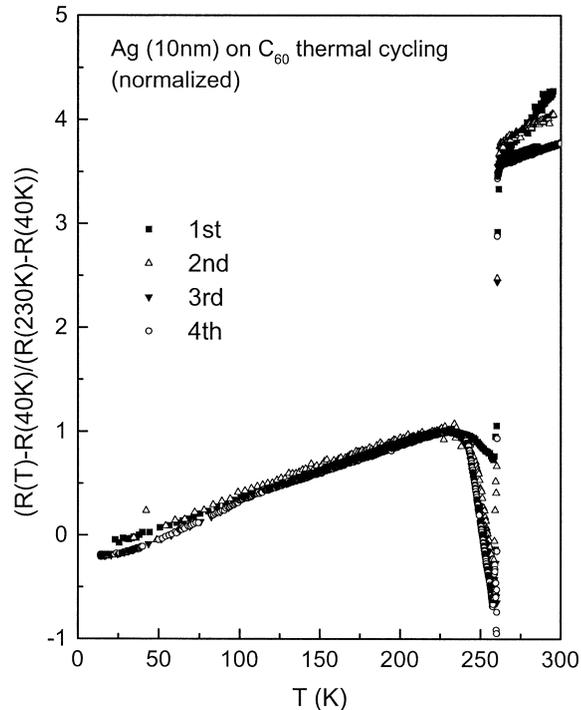


Fig. 4. The data of Fig. 2(a) rescaled according to the strain gauge model.

overlooks interesting physics. The mechanism by which the resistive sensitivity of the film is amplified is not established. While SEM characterization implicates film granularity, this feature alone does not guarantee amplification. Indeed, with the exception of the platinum curve, the data presented show positive dR/dT at low temperature, demonstrating that the continuous limit (insulating islands in a conducting matrix) is appropriate here. In this limit, away from the percolation threshold, extraordinary sensitivity to differential thermal expansion is not expected.

However, the biggest failing of the strain gauge model comes in the temperature range 240–260 K, which this discussion has until now ignored. The lattice constant of C_{60} is thought to be a monotonically increasing function of temperature, which makes it difficult for this mechanism to explain the region of negative dR/dT seen in the range 240–260 K. The appearance at 261 K of a resistance lower than the residual resistance, also unanticipated by this simple model, is even more striking. As illustrated by Fig. 2(a), the dip resistance remains relatively constant with thermal cycling, as compared with the resistance away from the ROT. The trivial explanation of macroscopic, temperature-dependent, nested currents has been tested with auxiliary measurements featuring rapid switching through different current/voltage four-probe configurations [10], and no evidence for such spurious effects is seen. Thus, at the ROT a new interaction seems to dominate the conductance of the film.

A more complete understanding of these resistive anomalies, particularly the 261 K dip, might reveal interesting phenomena. Exotic superconductivity has been apparently excluded, as we have found that these anomalies are independent of magnetic field up to 4.6 kG. We have also searched for evidence of critical exponents near the ROT, but the available data are inadequate for such analysis. Charge transfer between various metallic films and C₆₀ crystals has been widely reported [11,12], and two groups have reported anomalous conductance enhancements at room temperature in layered structures of metal films and C₆₀. [12–14]. They suggest that charge transfer creates an additional conduction band in the interfacial monolayer of C₆₀. Structural transitions of the C₆₀ crystal might perturb this two-dimensional channel, creating the resistance anomalies reported here. It is also possible that our 261 K anomaly is related to a proposed [15] intermediate phase that occurs in narrow temperature range around 261 K, or an unusual electron–phonon scattering effect. Interestingly, conductance peaks have been observed at phase transitions in other exotic materials [16].

In summary, we have measured the $\rho(T)$ behavior of different metal films on C₆₀ crystals as a function of thermal cycling and film thicknesses. We find features that correlate with structural phase transitions of C₆₀ crystals, thus demonstrating that metallic films can be sensitive probes of the underlying phase transitions of C₆₀ crystals. Finally, we see a dramatic resistivity dip near the ROT of C₆₀, which is unexplained by our simple model and may be evidence for a novel interaction.

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