

Susceptibility Discontinuity in Single Crystal C₆₀

Weili Luo and Hao Wang

Department of Physics, University of Central Florida, Orlando, Florida 32816

Rodney S. Ruoff

Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

Jerzy Cioslowski

Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306

Steven Phelps

Department of Physics, Stanford University, Stanford, California 94305

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Magnetization of a large single C₆₀ crystal was measured as functions of applied field and temperature. At $T = 260$ K, a discontinuity in susceptibility was observed. The relative change in total moment is 1.2%, independent of applied field to within experimental accuracy. This discontinuity is attributed to the change in the intramolecular geometry at the orientational order-disorder transition. This is the first experimental demonstration that the cooperative phase transition affects the magnetic susceptibility of a single molecule.

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Despite the vast research activity on thermodynamic, electronic, and optical properties of fullerenes, study of the magnetism of these materials is still at an early stage. Kroto *et al.* have first speculated on the presence of ring currents in the C₆₀ molecule [1]. Elser and Haddon have shown theoretically that the magnetic susceptibility of the C₆₀ molecule is small and slightly diamagnetic [2], which has been confirmed experimentally by Ruoff *et al.* and Haddon *et al.* on powdered samples [3, 4].

There are two types of bonds in an isolated C₆₀ molecule, the bond joining hexagon and pentagon with length of 1.46 Å, and the bond joining neighboring hexagons with length of 1.40 Å [5]. The shorter bond is electron rich relative to the longer bond [6]. The ordered phase in C₆₀(s) has electron rich bonds of one C₆₀ facing electron deficient pentagons of neighboring molecules, and vice versa [7]; that is, short-ranged intermolecular Coulomb interactions are present. These Coulomb interactions, together with the primary van der Waals interactions, give rise to a simple cubic structure for the low temperature ground state with *Pa3* symmetry [6]. In this phase a large fraction of the C₆₀ molecules are in an orientationally ordered state. At $T = 260$ K, C₆₀(s) undergoes a first-order phase transition. The high temperature phase is a plastic crystal phase, with the C₆₀ molecules rotating almost freely [8]. How the ordering transition affects the magnetic susceptibility has not yet been addressed.

In this Letter, we report our results on the magnetization of a large single crystal of C₆₀ and the first observation of a discontinuity in susceptibility at the orientational ordering transition [9]. We will show that measurement of the magnetic susceptibility is a sensitive technique for

probing the local environment of a single molecule at the orientational ordering transition. We attribute the discontinuity in magnetic susceptibility to the change in intramolecular geometry of individual C₆₀ molecules that accompanies the orientational order-disorder transition, as discussed further below.

Experiments were performed on a pure single C₆₀ crystal with mass of 13.3 mg. The crystal was grown using a vapor deposition technique which capitalizes on slight local minima in the temperature gradient across the growth ampoule employed [10]. The crystal has never been exposed to air and has a cylindrical disk shape with a thickness of 1 mm and diameter of 3 mm. Magnetic moment was measured with a Quantum Design SQUID magnetometer at the University of Central Florida. Because the change in magnetization was close to the baseline resolution of the magnetometer, care was needed to design the sample holder. A straight piece of heat shrink tube was used as the sample holder, having a length of 6 cm and i.d. of 3 mm. Because the i.d. of the tube was very close to the diameter of the C₆₀ crystal, the sample was held in the center of the heat shrink tube purely by friction. The C₆₀ crystal was weighed and transferred to the holder from a sealed glass tube in a glove box with only helium gas present. The signal from the sample holder was over 100 times smaller than the sample signal in temperature range measured.

The total magnetic moment m vs applied field at $T = 260$ K is shown in Fig. 1. A linear relation is obtained between m and H , and crosses zero at $H = 0$ G, which demonstrates that this crystal is free of impurities that have evidently been present in previous studies of the

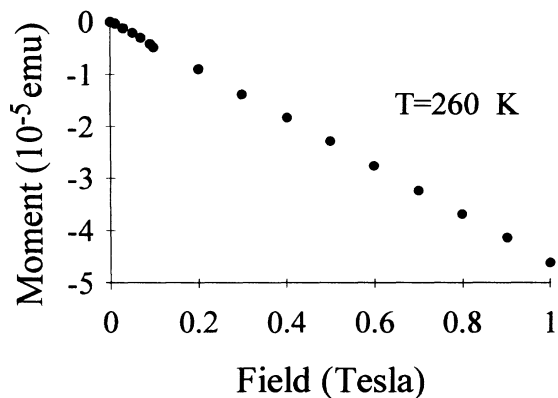


FIG. 1. Total magnetic moment, m , of the single crystal C_{60} as a function of applied field. The linear relation between m and H which passes through $H = 0$, indicates a negligible amount of paramagnetic impurities. The susceptibility, from the slope of the straight line, is $\chi = -4.6 \times 10^{-9}$ in cgs unit.

magnetic susceptibility of $C_{60}(s)$ [3,4]. The slope in Fig. 1 gives a susceptibility $\chi = -4.6 \times 10^{-9}$ in cgs units. The mass susceptibility is thus -3.4×10^{-7} , in agreement with room temperature values previously obtained on powder samples [3,4]. We have measured the temperature dependence of the susceptibility and found that the change of χ from 4 to 300 K is only a few percent. Therefore, the paramagnetic upturn at low temperature seen in previous studies is likely due to oxygen. An important separate result of our study is the proof, from the absence of a paramagnetic upturn in the low temperature susceptibility, that large crystal samples of C_{60} can be prepared which are *absolutely free of oxygen*.

In Fig. 2, we present the temperature dependence of the susceptibility from 240 to 290 K. A discontinuity at $T = 260$ K is clearly visible. Similar results have been obtained for different fields. Essentially, to within our error bar, the relative change $\Delta\chi/\chi$ is independent of field as shown in Fig. 3.

As pointed out by Wunderlich and co-workers, C_{60} can be classified as a plastic crystal, because the entropy change of the orientational ordering transition is similar to other plastic crystal systems [11]. As an aid to understanding the 260 K discontinuity in $\chi(T)$ of C_{60} , $\chi(T)$ was obtained for a sample of pure adamantane, $C_{10}H_{16}$. Adamantane undergoes a structural transition at 209 K between a high temperature fcc structure (in which the adamantane molecules rotate almost freely) and a low temperature body-centered tetragonal structure in which the individual molecules are orientationally ordered with respect to each other [12,13]. The percentage change in χ observed in adamantane at the ordering transitions is $\Delta\chi/\chi = 2.3\%$ (data not shown). Adamantane is a saturated alkane and cannot contain ring currents.

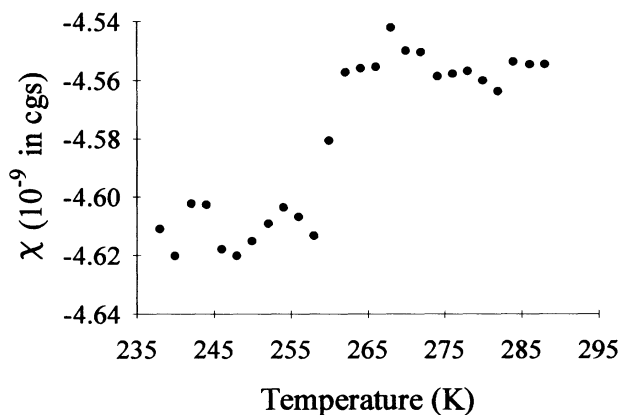


FIG. 2. Susceptibility χ vs T at $H = 1$ T for $T = 235$ K to $T = 290$ K. A "jump" occurs at $T = 260$ K, where the transition from the orientational disordered state to ordered state happens. The relative change, $\Delta\chi/\chi$ at $T = 260$ K is equal to 1.2%. The susceptibility can be considered to be independent of the temperature below and above the structural transition temperature, $T_c = 260$ K, which demonstrates that oxygen is entirely absent in the C_{60} crystal.

In order to obtain a semiquantitative estimate for the observed discontinuity in magnetic susceptibility, we carried out calculations on the magnetic shielding at the center of the C_{60} molecule. The shielding is known to be approximately proportional to the magnetic susceptibility of the fullerene cage [2]. Two GIAO CPHF calculations [14] have been performed. The first calculation employed the MNDO optimized geometry [15] of C_{60} (the bond lengths of 1.400 and 1.474 Å), whereas the second one utilized the HF/DZP geometry [16] (the bond lengths of 1.374 and 1.449 Å). The bond alteration is approximately identical in both geometries, but the bonds in the latter case are about 1.8% shorter.

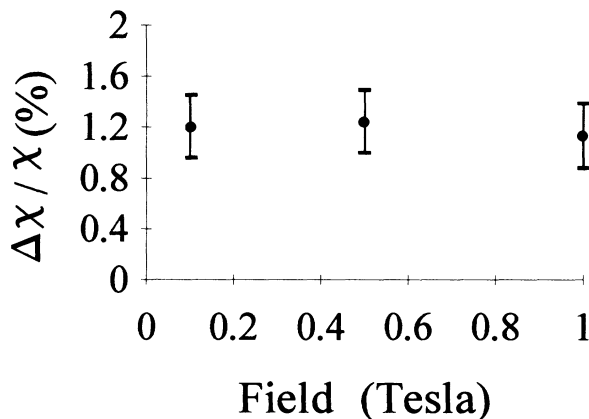


FIG. 3. The relative change of the magnetic susceptibility at 260 K, $\Delta\chi/\chi$, as a function of applied field, H , is independent of the field to within our experimental error bar.

Comparison of the computed shielding tensors revealed their *extraordinary sensitivity* to the geometry of C_{60} , as demonstrated by their relative difference of about 30%. This means that a change of only 0.07% in the bond lengths should be sufficient to alter the magnetic shielding by 1.2% and the susceptibility by a similar amount. Changes of this order can be certainly expected to accompany the phase transition at $T = 260$ K, as the vibrational frequencies of the fullerene cages in solid C_{60} are known to experience the corresponding discontinuities of $2-11\text{ cm}^{-1}$ or 0.3%–0.8% relative shift [17–20]. In fact, direct measurement of a range of bond lengths at $T = 5$ K by neutron diffraction shows there no longer exist only two unique bond types, but rather a wide range, with the longer “single” bonds ranging from 1.420 to 1.487 Å and the shorter “double” bonds ranging from 1.366 to 1.412 Å [7].

We therefore are confident that the observed discontinuity in magnetic susceptibility of solid C_{60} can be explained with the change in cage deformation alone. This mechanism best explains the results for both systems studied, $C_{60}(s)$ and adamantane. Our results show that this intramolecule change due to the structural transition is not unique in the system with ring currents (C_{60}) because adamantane does not have ring currents. We point out that the relative change in χ is larger for adamantane than for C_{60} at the ordering transition for each molecule, 2.3% (adamantane) vs 1.2% (C_{60}). The larger relative crystal volume change [9% for adamantane(s) [13] vs 0.9% for $C_{60}(s)$ [21]] and the change from having the center-of-mass of each adamantane molecule located on an fcc lattice to being located on a bcc tetragonal lattice (larger anisotropy), may explain the larger relative change in χ for adamantane.

In conclusion, a susceptibility discontinuity ($\Delta\chi/\chi = 1.2\%$) is observed at the orientational ordering transition in a large single crystal of C_{60} . A similar susceptibility discontinuity is observed at the orientational ordering transition of adamantane ($\Delta\chi/\chi = 2.3\%$). These measurements are the first to monitor the influence of the cooperative orientational ordering on the magnetic susceptibility of molecules in plastic crystal systems. The discontinuity in χ is explained by small intramolecular geometry changes which occur at the phase transition.

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