Orientational order in A_3C_{60}: Antiferromagnetic Ising model for the fcc lattice.

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By analysis of the electronic contribution to the binding in A_3C_{60}, we show that the problem of orientational ordering can be mapped onto the fcc nearest-neighbor antiferromagnetic Ising model with J at the order of 100K. For $T < 1.76J$, the system should be found in a state which is antiferromagnetically ordered in two dimensions and disordered in the third. This is not inconsistent with present X-ray powder data. We find that the low-temperature conduction-band structure closely resembles that of the simplest antiferromagnetically ordered (so-called bi-directional) crystal.

After the discovery of superconductivity in solid A_3C_{60}[1], it became important to figure out the low-temperature crystal structure. It was found that the C_{60}–molecules are on an fcc lattice and that the alkali ions fill the octahedral and tetrahedral pores[2]. Each molecule takes one of two possible orientations. In both of them, 6 of the 30 double bonds are parallel with the cubic axes and the two orientations are transformed into each other by any $\pi/2$-rotation around any of the cubic axes. That only these two orientations are possible, was established experimentally[2] and can also be understood from consideration of the space requirements of the alkali ions. The X-ray pattern at room temperature was found consistent with a random occupation of each site by a molecule of either orientation[2]. Such a 3-dimensional, orientational disorder would have tremendous effects on the electronic properties, as demonstrated by a theoretical calculation[3]. The X-ray experiment does not distinguish between static and dynamic disorder, but NMR[4] showed that on a 50μsec time-scale, the disorder in K_3C_{60} is static for temperatures below ≈270K, and dynamic above.]

A theoretical attempt to predict the orientational ordering of fullerenes at T=0, was undertaken by Gunnarsson et al.[5] who estimated structural energies using a tight-binding model with the 60 radial carbon p-orbitals per molecule as basis. For doped C_{60}, the lowest energy was obtained for the so-called bi-directional structure (BDS). This is a crystal in which the orientation is the same for all molecules in each (100)–plane, and alternates between neighboring planes. The BDS thus corresponds to the tetragonal CuAu-structure and has space group $P4_2/mnm$. Compared with the uni-directional structure (UDS, $Fm\bar{3}$), where all molecules have the same orientation, the BDS turned out to be energetically favorable by $\sim 10^3$ K/molecule.

In this paper we shall argue, that the low-temperature structure of K_3C_{60} is not 3-dimensionally disordered, but bi-directionally ordered in two dimensions and disordered in the third. The 2-dimensional order is estimated to melt at about 200K in K_3C_{60}. What NMR observes above 270K, is merely that the orientational life-time becomes shorter than the 50μsec sampled by this technique. We shall see, that with X-ray scattering, the low-temperature 1-dimensionally disordered structure (1DDS) is difficult to distinguish from the high-temperature 3-dimensionally disordered structure (3DDS). Of the infinitely degenerate 1DDS, one coincides with the BDS. Its conduction-band, discussed in Ref.[6], will be shown to be representative of the 1DDS.

First, we show that the orientational energy of A_3C_{60} can be approximately described by the fcc nearest-neighbor (nn) antiferromagnetic Ising model (AFIM),

$$E = J\frac{1}{N}\sum_{\langle ij\rangle}\sigma_i\sigma_j \equiv JS, \qquad (1)$$

where E is the energy per molecule, N is the number of molecules, the sum is over all nn pairs (bonds), and σ_i is ± 1 depending on the orientation of the molecule at site i. For the fcc lattice, the Ising sum S is restricted to the range $-2 \le S \le 6$. To demonstrate the validity of (1), we use the approach of the the density-functional force theorem[7] and the Harris functional[8]. This means that to each C_{60} molecule (and each alkali atom), we assign a charge density which is kept fixed as the orientations of the molecules are changed. Then, to first order in the (small) deviation between this trial

density $\tilde{\rho}(\mathbf{r})$ and the true density, the difference in energy between two configurations equals the difference in the eigenvalue sum, in the Madelung interaction for the trial density, and in the exchange-correlation term $\int d^3r\tilde{\rho}(\mathbf{r})\{\varepsilon_{xc}[\tilde{\rho}(\mathbf{r})]-v_{xc}[\tilde{\rho}(\mathbf{r})]\}$. Here the eigenvalues correspond to the LDA potential calculated for the trial density.

The exchange-correlation term is a pair-wise interaction, if we can assume that in each point, the charge density can be considered to be a superposition of, at most, two molecular charges. For solid C_{60}, the ranges of space where this approximation is not satisfied, involve a very small fraction of the charge. The Madelung interaction between A^+ and C_{60}^{3-}, and between the A^+–ions, is the same for the two orientations and is therefore irrelevant. The Madelung interaction between the C_{60}^{3-} molecules can be decomposed pairwise and, due to the large distance ($\approx$7Å) between the closest atoms on the next nearest-neighbor (nnn) molecules, and to the high multipolarity of the C_{60} molecule, only the interaction between the nn molecules needs to be kept. Hence, it has the form of the AFIM (1).

For the one-electron energy sum, we first use the tight-binding (TB) nn-molecule approximation, which excellently reproduces the density-functional energy bands[5,6]. The contribution from the full bands, plus the one from the *position* of the half-filled t_{1u} band, can be accurately calculated using second-order perturbation theory, and can therefore be decomposed into pair-interactions[5]. We tested this numerically by performing TB-calculations with the basis of 60 radial carbon p-orbitals per molecule (rad-AO basis)[9] for a sc unit cell with all four, with three, or with two of the molecules having the same orientation. Both energy differences yield the *same* contribution (70K) to J when fitted by the AFIM (1).

The contribution from the *broadening* of the t_{1u} conduction band can also be approximated by (1). A crude argument goes as follows: The energy of the 3 electrons in the t_{1u} band is roughly $-3W/4$, where the bandwidth W ($\approx$0.5eV) is proportional to the square-root of the second energy-moment. Now, the latter is the sum of the t_{1u} hopping integrals squared, with the integrals for hopping between parallel molecules being about 10% smaller than the integrals for hopping between perpendicular molecules[5]. As a result (see Eqs.24–27 in Ref.[6]), the orientational energy may be expressed as: $E_W \approx -3W/4\left(\sqrt{1-0.1S/6}-1\right)$, where W is now the bandwidth for zero Ising sum. Expansion of the square root finally leads to the AFIM (1) with $J \approx 0.1W/16 \approx$40K. An extensive numerical test was done by performing TB band-structure calculations for a $5\times5\times5$ sc cell with 500 molecules of randomly chosen orientations, using as basis just the three t_{1u}-molecular orbitals per molecule (single-MO basis)[10]. The calculated band-structure energies are shown by the filled dots in Fig. 1 as a function of the Ising sum. They follow a straight line, i.e. the AFIM (1), fairly well. Even the energies shown by the open dots numbered 1–5 for ordered, short-period configurations are close to the straight line[11]. Comparison between points 1 and 2 renders an estimate of the band-broadening contribution to the nnn interaction, which is seen to be antiferromagnetic and of order 1K.

We have thus demonstrated that the total orientational energy is well represented by the fcc nn AFIM (1). The total value of J, calculated as one eighths the energy-difference between the uni- and bi-directional structures with the TB rad-AO scheme, is 95K[9]. The value of J has also been calculated with the full-potential LMTO-LDA method, which includes effects neglected in the tight-binding calculation (exchange-correlation effects and Madelung interactions). We find that the result, $J = 110$ K[12], is similar to the tight-binding result.

The fcc nn AFIM has been studied intensively since the beginning of the 60's[13], and it is a classical example of a frustrated anti-ferromagnet. Danielian[14] was the first to describe the ground state: Each (001)–plane has AF–order such that all 4 nn's, at $(\pm\frac{1}{2},\pm\frac{1}{2},0)$, of a given site, (0,0,0), have the opposite spin. The next AF (001)–plane can now be generated from the first, either by the translation $[\frac{1}{2},0,\frac{1}{2}]$, which we shall refer to as x, or by the translation $[0,\frac{1}{2},\frac{1}{2}]$ (y). In both cases, 2 of the 4 additional nn's will have the same spin and 2 will have the opposite spin. For *any* stacking of the planes, e.g. *..xxyxyy..*, each site will therefore have 8 nn's with the opposite, and 4 nn's with the same spin. Hence, the ground state is infinitely degenerate with $E = -2J$. While the BDS is *one* of the ground states (*..xxxx..*)[15], the more general ground state is disordered in the z-direction. This is what we call the 1DDS. Next-nearest neighbor interactions will favor an ordered structure (the BDS, in case of ferromagnetic nnn interactions, and the *..xyxy..*-structure, in case of anti-ferromagnetic nnn interactions), but such interactions appear to be only of order 1K (see Fig.1). Since only disorder in 1D is permitted, the entropy per site is zero at $T = 0$ and increases slowly with temperature. For the nn AFIM, the BDS is stabilized over the 1DDS at all $T \neq 0$, but the free-energy difference between the average 1DDS and the BDS remains order $10^{-4}J$[16], and we therefore expect the low-temperature structure of A_3C_{60} to be a metastable 1DDS, or possibly the ordered *..xyxy..*-structure. At finite temperature, the 1DDS breaks into antiphase domains in such a way that the domain walls have zero energy. The energy of a domain edge is $8J$ per fcc lattice constant (a) and that of a point defect is $8J$. The number of defects therefore grows as $\exp(-8J/T)$ at low temperature[14,16,17]. At $T_N \approx 1.76J \sim$200K the long-range AF order is lost even within the planes; the "heat of melting" is $\Delta E \approx 0.5J \approx 50$ K$\approx$4 kJ/Mole[16,17].

A difference between the thermodynamics of the fcc nn AFIM and that of orientation-flips in A_3C_{60}, is that for the latter there is a potential barrier B. Therefore, at temperature T, an orientation has a life-time $\tau(T) \approx \nu^{-1}\exp(B/T)$, where $\nu \approx 10^{12}$/sec is the frequency of the rotational phonons[18]. Since for K_3C_{60},

NMR indicates that $\tau(270\text{K}) \approx 50\mu\text{sec}$[4], we estimate that $B \approx 4800\text{K}$. This means that the orientational life-time $\tau(T_N)$ at the Neel temperature is about 1sec. In Rb_3C_{60}, NMR shows no dynamical disorder even at room temperature[4] so that for this material, the orientational life-time may be so long that the low-temperature structure depends crucially on the details of the preparation.

How would the predicted low-temperature 1DDS manifest itself in X-ray scattering, and could it be distinguished from the 3DDS? The electron density of the solid may be expressed as:

$$\sum_{\mathbf{R}} \bar{\rho}(\mathbf{r}-\mathbf{R}) + \sum_{\mathbf{R}} \sigma_{\mathbf{R}} \tilde{\rho}(\mathbf{r}-\mathbf{R}), \qquad (2)$$

where $\bar{\rho}(\mathbf{r})$ is half the sum of, and $\tilde{\rho}(\mathbf{r})$ half the difference between, the electron densities of a single molecule for the two orientations, $\mathbf{R}$ are the fcc lattice translations, and the scattering from the K-ions is neglected. The first term is the fcc-periodic density from the orientationally averaged molecules and $\sigma_{\mathbf{R}}$ in the second term are the variables defined in (1). Since $\langle \sigma_{\mathbf{R}} \rangle = 0$, the X-ray intensity takes the form:

$$\left|\bar{f}(\mathbf{k})\right|^2 \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} + \left|\tilde{f}(\mathbf{k})\right|^2 \sum_{\mathbf{R}} \langle \sigma_{\mathbf{0}} \sigma_{\mathbf{R}} \rangle \, e^{i\mathbf{k}\cdot\mathbf{R}}. \qquad (3)$$

with no cross-terms. Here, $\bar{f}(\mathbf{k}) \equiv \int \bar{\rho}(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r}) d^3r$ is half the sum of, and $\tilde{f}(\mathbf{k})$ is half the difference between, the form factors of the molecule for the two orientations. The X-ray intensity (3) thus consists of two terms: the Bragg scattering from an fcc crystal of orientationally averaged molecules ($\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = 4(2\pi/a)^3 \sum_{\mathbf{G}} \delta(\mathbf{k}-\mathbf{G})$, with $\mathbf{G}$ being the fcc reciprocal lattice points), plus the scattering from the orientational fluctuations. Orientational order will therefore show up only in the second term. For the 3DDS, $\langle \sigma_{\mathbf{0}} \sigma_{\mathbf{R}} \rangle = \delta_{\mathbf{0},\mathbf{R}}$, so that the second term is a diffuse 3D-background of density $\left|\tilde{f}(\mathbf{k})\right|^2$. For the 1DDS, $\langle \sigma_{\mathbf{0}} \sigma_{\mathbf{R}} \rangle = \pm\delta_{0,R_z}$, where the +sign holds for $(R_x, R_y) = (n_x, n_y)a$, and the −sign for $(R_x, R_y) = (n_x+\frac{1}{2}, n_y+\frac{1}{2})a$, and the n's take all integer values. In this case, $\sum_{\mathbf{R}} \langle \sigma_{\mathbf{0}} \sigma_{\mathbf{R}} \rangle \, e^{i\mathbf{k}\cdot\mathbf{R}} = 2(2\pi/a)^2 \sum_{\mathbf{G}_{2D}} \delta(\mathbf{k}_{2D}-\mathbf{G}_{2D})$, with $\mathbf{G}_{2D} \equiv (m_x, m_y)2\pi/a$ and $m_x + m_y$ odd. The only way in which the development of 2D AF-order below T_N would manifests itself, is therefore as a condensation of the diffuse 3D-background into 1D-strings running in the [001]–direction, between the fcc reciprocal-lattice points, which would further condense into additional Bragg peaks for the 3D–ordered BDS and ..$xyxy$.. structure. The scattering intensity of each fcc Bragg peak is unchanged. In a powder diagram, the 1DDS can therefore hardly be detected, especially when $\left|\tilde{f}(\mathbf{k})\right|^2 \ll \left|\bar{f}(\mathbf{k})\right|^2$. The difference in the diffuse background can hardly be detected in X-ray scattering, because the relevant wave vectors are too large, $\gtrsim 3\text{Å}^{-1}$, but can detected in neutron scattering. The published data[19] are more compatible with the 3DDS, but it is not clear how well the sample had been annealed.

How would the 1DDS structure affect the electronic properties? Most published electronic-structure calculations are for the uni-directional structure (UDS) and exhibit a density-of-states peak near the Fermi level[20]. In the 3DDS, this peak is completely smeared out and, as a consequence, $N(\epsilon_F)$ is reduced by about 40%[3]. This would have important implications for the superconductivity. For the BDS, the $N(\epsilon)$-shape is quite different from that of the UDS, but the Fermi level again falls near a peak and $N(\epsilon_F)$ is even a bit larger than in the UDS, although the conduction band is wider[6]. We have now performed TB single-MO calculations for five random stackings of one hundred AF (001)–layers. The resulting density of states for the 1DDS is compared with that of the BDS in Fig. 2, and the similarity is striking. The following facts may provide some understanding of why: Two neighboring (001)–layers always define a BDS–crystal and the probability that this crystal continues l inter-layer spacings upwards, is $1/2^l$. Therefore, the average thickness of the BD-domain surrounding any layer is $2\langle l \rangle = 2\sum_{l\geq 1} l/2^l = 4$ in units of the inter-layer spacing $a/2$, i.e. as large as 29Å. It is also interesting to note that the overall shape of $N(E)$ in the 3DDS model considered by Gelfand and Lu[3] is much closer to the BDS than to the UDS (Fig. 2). Finally we note, that even at $T = 2.8J \sim 300\text{K}$, the energy of the AFIM is still $-J$[17], so that about half the molecules have the same local coordination as at *T=0.* Even at room temperature, the electronic structure is therefore intermediate between those of the BDS and the 3DDS.

The electrical resistivity in the normal state might distinguish between the 1DDS and the 3DDS, provided that the intrinsic metallic resistivity is measured. Unfortunately, the experimental situation does not allow firm conclusions about the intrinsic resistivity[21]: Very different temperature dependencies have been reported, and the value of the room-temperature resistivity scatters from 2 to 5 mΩ cm, which corresponds to the mean-free path being less than the fcc lattice parameter, i.e., beyond the minimal metallic conductivity. 3-dimensional orientational disorder is calculated to provide a resistivity of merely 0.3mΩ cm[22] and phonons would, in the high-temperature limit, cause the resistivity $\rho \approx 8\pi^2 \hbar \omega_p^{-2} k_B T \lambda$, which is about 3λ $\mu\Omega$ cm /K$\sim$1mΩ cm at room temperature, taking $\omega_p = 1.2$ eV.

To summarize, we have shown that the problem of orientational ordering in K_3C_{60} can be mapped onto the fcc nearest-neighbor Ising model with an antiferromagnetic coupling constant $J \approx 100\text{K}$. The ground state is 2-dimensionally anti-ferromagnetically ordered and 1-dimensionally disordered. This structure is difficult to distinguish by powder X-ray scattering from the 3-dimensionally disordered high-temperature structure. The conduction-bands for the two structures are very different. That of the low-temperature structure is

well represented by the conduction band of the so-called bi-directional crystal with space group $P4_2/mnm$. The 2-dimensional long-range order vanishes in a first-order phase transition with $T_N \approx 1.76J$. The barrier between orientational flips appears to be large, of order 5000K.

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[10] The TB single-MO calculations of the present paper used the *conv.*-values from tables II and III of Ref.[6] for the hopping integrals and the lattice constant 14.10Å.

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FIG. 1. t_{1u} band-broadening energy vs. Ising sum calculated using the single-MO approximation[6] and a sc cell containing 500 molecules with randomly chosen orientations (filled dots). Open dots: Ordered short-period structures, (1) BDS=CuAu=AF (100)-planes ordered like *..xxxx..* as described in the text, (2) *...xyxyxy..*, (3) Cu_3Au, (4) AF MnO=ferromagnetic (111)-planes of alternating orientation, (5) uni-directional=ferromagnetic. Cross: 1DDS.

FIG. 2. Density of states of the t_{1u}-band in the 1-dimensionally disordered structure (Ising ground state) and in the completely disorder structure, compared to the crystalline bi-directional structure. For the former, the width of the line corresponds to the statistical error. The t_{1u}-TB model was used[6].