Endohedral Fullerites: A New Class of Ferroelectric Materials

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Endohedral fullerites, composed of periodic lattices of endohedral complexes with polar molecules trapped inside the C_{60} cluster, constitute a new class of ferroelectric materials and the first practical realization of ideal electric dipolar lattices. In these substances, interactions between the partially screened and freely rotating dipole moments of the guest molecules give rise to dipole-ordered low-temperature phases. The respective transition temperatures for the endohedral fullerites with LiF, LiCl, NaF, and NaCl as the guest molecules are estimated to be at 25, 36, 51, and 60 K, respectively.

PACS numbers: 77.80.-e, 64.60.Cn, 65.40.Hq

The known ferroelectric materials are traditionally divided into two classes that reflect the mechanisms responsible for the transitions to the low-temperature phases [1]. The first class encompasses many ionic crystals in which the individual ions move in potentials with several closely spaced minima. In these displacive-type ferroelectrics, of which barium titanate BaTiO₃ is a well-known example, the high-temperature phase is associated with the vibrationally averaged positions of ions, whereas the low-temperature (anti)ferroelectric phase corresponds to ions at the individual minima of the potential energy hypersurface. On the other hand, in the order-disorder-type ferroelectrics, such as potassium dihydrogen phosphate KH₂PO₄, the appearance of the low-temperature phase is directly linked to an order-disorder transition that often involves infinite networks of hydrogen bonds.

In this Letter, we predict the existence of a new class of ferroelectric materials composed of the endohedral complexes [2] in which polar molecules are trapped inside the C₆₀ cluster. Although macroscopic quantities of these endohedral fullerites [3] have yet to be isolated, there is a plethora of both direct and indirect experimental evidence that confirms their existence. In particular, endohedral complexes with one [4,5] or two [6] noble gas atoms (He, Ne, and Ar) as the guests have been observed in collisional insertion experiments. Complexes with metals such as La, Ni, Na, K, Rb, and Cs [7] have also been detected among the products of laser or arc ablation of graphite rods impregnated with metal salts. Even more notably, in a very recent publication, endohedral complexes (primarily of the C_{60} cluster) with small polar molecules (including CaCl, CeCl, NaCl, and NaI) have been reported [8].

Previous calculations [2(b)] demonstrated the absence of any significant (the activation energy of ca. 20 cal/ mol) barriers to rotation for sufficiently small guest molecules inside the C_{60} cage. This observation, together with the fact that the cage screens the dipole moments of the guest molecules only partially [2,9], means that the endohedral fullerites can be regarded as the first practical realization of ideal electric dipolar lattices. The dipolar lattices have been the subject of several theoretical studies [10-15] and have been found to correctly describe many substances whose thermodynamic properties are determined mostly by magnetic dipole-dipole interactions [16]. On the other hand, ideal lattices with *electric* dipole-dipole interactions have not found, until now, any applications to real systems due to the presence of close packing in molecular crystals that hinders free rotation of molecular dipoles [17].

The recent x-ray-diffraction measurements [18] show that solid C₆₀ possesses an fcc lattice with $a_0 = 14.2$ Å and four C_{60} molecules per unit cell. Below 249 K the lattice becomes simple cubic (sc) due to rotational freezing of the individual C_{60} cages and a_0 decreases slightly. Since the dipole-dipole interactions in endohedral fullerites are expected to be rather weak, one may safely assume the lattices of these substances to be identical with that of the pristine fullerite. Moreover, since screening of the internal dipole moments by the C_{60} cage is isotropic [2(b),9] and therefore insensitive to the rotational motion of the C_{60} molecule, one may use the high-temperature fcc lattice in the modeling of the phase transition associated with the dipole-dipole interactions. The dipolar lattice of the fcc type is known to undergo transition to a low-temperature dipole-oriented phase, although there appears to be disagreement in the literature [10-12] whether this phase is ferroelectric (possibly with domains), or ferroelectric/antiferroelectric depending on the sample shape.

It is clear from the dimensional analysis that the transition temperature of the dipolar lattice T_0 is proportional to the characteristic temperature T^* ,

$$T_0 = \alpha T^*, \quad T^* = \mu^2 (k a_0^3)^{-1}.$$
 (1)

In Eq. (1), μ is the dipole moment at each lattice node, and k is Boltzmann's constant. The dipole moment μ is related to the dipole moment of the guest molecule *in* vacuo, μ_0 , by the relation

$$\mu = (1 - \sigma)\mu_0, \qquad (2)$$

where σ is the dipolar screening constant of the C₆₀ cage [2,9]. The proportionality constant α [Eq. (1)] has to be

either computed by numerical simulations, or calculated with the help of an approximate theoretical treatment. In order to obtain a semiquantitative estimate of α and gain some insight into the character of the transition, we calculated the values of the configurational constant-volume heat capacity c_v at several temperatures for a cluster composed of 63 freely rotating dipoles located at the nodes of the fcc lattice spanning a cube extending two unit cells in each direction. The evaluation of the average values that enter the fluctuation formula for c_v was accomplished by a direct numerical integration over 126 rotational degrees of freedom. Reasonable accuracy (ca. 10% in the estimated T^* and c_v , see below) was achieved with 2×10^8 sampling points selected according to the Diophantine-like quadrature of Wozniakowski, which is a numerical method for evaluation of multidimensional integrals with the help of nonrandom grids [19].

The results of the aforementioned simulation are presented in Fig. 1. Despite the small size of the cluster, a well-formed anomaly in the heat capacity is predicted, with c_v reaching its maximum at T/T^* of ca. 6.3. The corresponding value of c_v is estimated at ca. 0.53 cal/K per mole of the C₆₀ molecules. The transition itself appears to be continuous and quite similar to that previously described [15] for the sc lattice.

We also calculated the dipolar screening constant σ for the C₆₀ cage using *ab initio* electronic structure methods [20] and obtained the value of 0.80 at the HF/6-31G level of approximation (which is a Hartree-Fock calculation with a basis set that can be considered essentially converged for this type of problem). Combining Eqs. (1) and (2), using $a_0 = 14.2$ Å, and assuming α to be equal to T/T^* at the maximum of c_c , this gives

$$T_0 = 0.63 \,\mu_0^2 \tag{3}$$

as the estimate for the transition temperature in K, the



FIG. 1. The dependence of the molar constant-volume heat capacity on the reduced temperature for a cluster of 63 freely rotating dipoles (see text). R denotes the gas constant.

dipole moment being expressed in D. With the dipole moments of the LiF, LiCl, NaF, and NaCl molecules estimated [21] at 6.3, 7.6, 8.1, and 9.8 D, respectively, this gives the values of 25, 36, 41, and 60 K for the transition temperatures of the respective endohedral fullerites. One should note that all of the above molecules are expected to fit easily inside the C_{60} cage, with the NaCl molecule being perhaps slightly hindered in its rotation.

When isolated, the endohedral fullerites will be found to possess properties significantly different from both the displacive and order-disorder ferroelectrics. First of all, as shown above, the transition temperatures of the endohedral fullerites are expected to be much lower than those of common ferroelectric materials. Second, since the onset of the ordered phase is not related to any vibrational mechanism, the isotopic effect is going to be absent in endohedral fullerites (except for solids with very low T_0 , in which quantum effects will play some role). On the other hand, since endohedral fullerites (like the C₆₀ crystals) are expected to be very compressible at low pressures [18] and the lattice constant enters the equation for T_0 in the third power, there is going to be a pronounced positive pressure effect on T_0 .

We acknowledge support from the National Science Foundation under Contract No. CHE-9015566, the Camille and Henry Dreyfus Foundation New Faculty Award Program, the Florida State University through time granted on its Cray Y-MP digital computer, the U.S. DOE through its Supercomputer Computations Research Institute, and the donors of the Petroleum Research Fund administered by ACS (Grant No. PRF 25076-G6).

- [1] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).
- [2] (a) J. Cioslowski and E. D. Fleischmann, J. Chem. Phys.
 94, 3730 (1991); (b) J. Cioslowski, J. Am. Chem. Soc.
 113, 4139 (1991).
- [3] Fullerite is a material composed of solid C₆₀, which is also known as [60] fullerene, see W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) 347, 354 (1990).
- [4] T. Weiske, T. Wong, W. Krätschmer, J. K. Terlouw, and H. Schwarz, Angew. Chem. Intern. Ed. 31, 183 (1992).
- [5] T. Weiske, D. K. Böhme, J. Hrusak, W. Krätschmer, and H. Schwarz, Angew. Chem. Intern. Ed. **30**, 884 (1991);
 K. A. Caldwell, D. E. Giblin, C. S. Hsu, D. Cox, and M. L. Gross, J. Am. Chem. Soc. **113**, 8519 (1991); M. M. Ross and J. H. Callahan, J. Phys. Chem. **95**, 5720 (1991).
- [6] T. Weiske and H. Schwarz, Angew. Chem. Intern. Ed. 31, 605 (1992).
- [7] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. C. Chibante, J. Fure, L. Wang, J. M. Alford, and R. E. Smalley, J. Phys. Chem. 95, 7564 (1991).
- [8] T. P. Martin, M. Heinebrodt, U. Näher, H. Gohlich, T. Länge, and H. Schaber, in *Clusters and Fullerenes*, edited by V. Kumar and T. P. Martin (World Scientific,

Singapore, 1992).

- [9] J. Cioslowski and A. Nanayakkara, J. Chem. Phys. 96, 8354 (1992).
- [10] J. M. Luttinger and L. Tisza, Phys. Rev. 70, 954 (1946).
- [11] M. Lax, J. Chem. Phys. 20, 1351 (1952); R. Rosenberg and M. Lax, J. Chem. Phys. 21, 424 (1953); R. L. Fulton, J. Chem. Phys. 62, 3676 (1975).
- [12] D. E. Sullivan, J. M. Deutch, and G. Stell, Mol. Phys. 28, 1359 (1974).
- [13] D. J. Adams and I. R. McDonald, Mol. Phys. 32, 931 (1976).
- [14] A. Erzan and G. Stell, Phys. Rev. B 18, 408 (1978).
- [15] S. Romano, Nuovo Cimento 7, 717 (1986).

- [16] T. Niemeyer, Physica (Utrecht) 57, 281 (1972).
- [17] The electric dipolar lattices have been used as a crude model for the order-disorder transition in hydrogen halides, see J. Frenkel, Acta Phys. Chim. U.S.S.R. 3, 23 (1935).
- [18] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denestein, J. P. McCauley, Jr., A. B. Smith, III, and D. E. Cox, Phys. Rev. Lett. 66, 2911 (1991).
- [19] H. Wozniakowski, Bull. Am. Math. Soc. 24, 185 (1991).
- [20] J. Cioslowski and K. Raghavachari (to be published).
- [21] We obtained these values for the bond lengths optimized at the HF/6-311G* level of approximation.