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FULLERENES AND ATOMIC CLUSTERS

Dielectric Properties of C_{60} Molecular Complexes

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Abstract—The permittivity ε of the molecular complexes $(BTX)C_{60}CS_2$, $(DAN)C_{60}(C_6H_6)_3$, and $(S_4N_4)_{1.2}C_{60}(C_6H_6)_{0.8}$ has been studied at 100 MHz. A maximum has been observed to appear in the temperature dependence ε(T) at $T \approx 90$ K, which can be assigned to freezing of the orientational disorder. A region of anomalous growth of ε with decreasing temperature has been found in the low-temperature range $T \le 25$ K, this feature being apparently sensitive to the actual packing pattern of C_{60} spheres in the molecular complex. © *2000 MAIK "Nauka/Interperiodica".*

1. Crystals of the C_{60} fullerene are known to exist in several structural modifications [1]. At high temperatures $T > T_I \approx 260$ K, the orientationally disordered fcc phase is stable, and a decrease of temperature below T_I induces a transition to a phase with a simple cubic lattice. This transition is accompanied by a strong suppression of orientational disorder, so that for $T < T_I$ two dominant orientations of C_{60} molecules survive. A further decrease of temperature down to $T_{II} \approx 90$ K transfers the fullerene crystal to a specific glassy state with a frozen orientational disorder, to leave about 17% C_{60} molecules in an energetically less favorable configuration [1].

The phase transitions at $T = T_I$ and T_{II} are accompanied by a sharp change in the relaxation time [2–4], which determines various physical properties of the fullerenes, including low-frequency permittivity. However, the available information on the temperature and frequency dependences of the permittivity ε(ω, T) are contradictory [1–3, 5]. For instance, there is no agreement on the absolute value of ε or the mechanism of dipole relaxation. The effect of oxygen impurity on the dielectric properties of C_{60} is likewise an object of current debate. Some authors [1, 2, 5] believe the oxygen impurity provides a dominant contribution and accounts completely for the specific features of ε(ω, T), whereas other studies suggest that the dielectric characteristics of the fullerenes relate to intrinsic properties and depend only weakly on impurities [3]. Viewed from an experimental standpoint, this problem is aggravated by the strong sensitivity of C_{60} films to the actual conditions of preparation and annealing [1–3, 5].

Molecular complexes of fullerenes with an organic donor compound could be promising for investigation of the physical mechanisms governing the dielectric relaxation of the fullerenes and related compounds [6–10]. Compounds of this type can exist in a variety of structures, namely, chain, layered, or structures with a 3D arrangement of C_{60} molecules. They are characterized by a small amount of charge transfer between the donor and the C_{60} molecule (such complexes are held together primarily through van der Waals polarization forces [7]). Besides, the present concepts consider the high-temperature rotation of C_{60} molecules in molecular complexes to be frozen [6, 8, 9]. It is essential that single crystals of C_{60}-based molecular complexes can be relatively large in size, which offers a possibility of making dielectric measurements on bulk crystals rather than on polycrystalline films (as is the case with pure C_{60}).

Thus investigation of C_{60}-based molecular complexes is of interest from the viewpoint of the key aspects of the problem of dielectric properties, which include orientational transitions, the effect of crystalline structure, and uncontrollable impurities.

2. For the study of the dielectric properties, we chose single crystals of the complexes $(BTX)C_{60}CS_2$, $(DAN)C_{60}(C_6H_6)_3$, and $(S_4N_4)_{1.2}C_{60}(C_6H_6)_{0.8}$ [where BTX stands for 9,9'-trans-bis(tellurium aksanthenyl), and DAN, for dianthracene]. The $(S_4N_4)_{1.2}C_{60}(C_6H_6)_{0.8}$ and $(DAN)C_{60}(C_6H_6)_3$ complexes possess a layered structure, with closely packed layers of the C_{60} molecules alternating with layers of the donor and solvent molecules [8, 9]. A characteristic building block of the $(BTX)C_{60}CS_2$ complex is chains of C_{60} molecules with spacings between the centers of ≈10.31 Å, which is larger than the van der Waals diameter of the C_{60} molecule, ≈10.18 Å. Thus, the C_{60} molecules in this complex practically do not interact with one another. The techniques used in the preparation of molecular fullerene complexes are described in detail in [8, 9].

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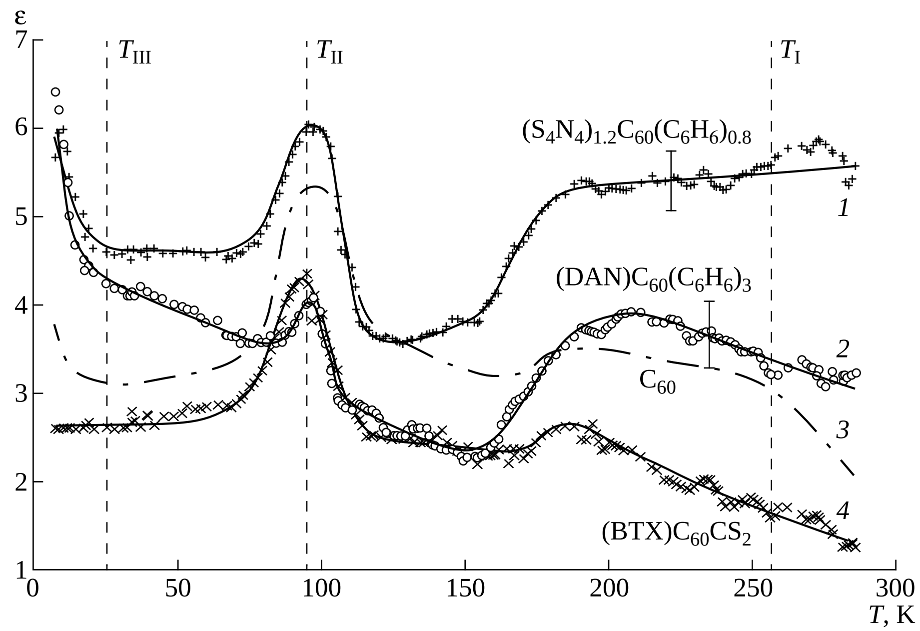

Temperature dependence of the permittivity measured at 100 MHz for various C_{60}-based molecular complexes. (*1*) $(S_4N_4)_{1.2}C_{60}(C_6H_6)_{0.8}$, (*2*) $(DAN)C_{60}(C_6H_6)_3$, (*3*) pure C_{60}, (*4*) $(BTX)C_{60}CS_2$. Dashed lines identify the characteristic temperatures T_I, T_{II}, and T_{III} (see text for explanation).

One also measured, for comparison, the dielectric properties of samples of pure C_{60} prepared by pressing from fullerene powder (similar samples were studied in [3]). The dimensions of the samples of C_{60} and C_{60}-based molecular complexes were typically $2 \times 1 \times 0.5$ mm.

The measurements of the low-frequency permittivity of C_{60} known from literature were made at frequencies $\omega/2\pi < 1$ MHz [1–4], which for $T < T_I$ corresponds to the case of $\omega\tau \ll 1$ (here τ is the characteristic time of orientational transitions, which in a general case, differs from that of dipole relaxation [3, 4]). It is obviously of interest to study the opposite situation of $\omega\tau \geq 1$, where one may expect a clearer manifestation of the effects associated with orientational disorder. Since $\tau \approx 2 \times 10^{-9}$ s in the region $T \approx T_I$, of the disorder-order transition [4], the condition $\omega\tau \approx 1$ corresponds to a frequency $\omega/2\pi \approx 100$ MHz. The permittivity measurements at the frequency $\omega/2\pi = 100$ MHz within the temperature range of 4.2 to 300 K were performed on a setup based on an HP4191A impedance meter, which is described in [11].

3. The temperature dependence of permittivity for various molecular complexes and pure C_{60} is shown graphically in the figure. Note the complex nonmonotonic character of the temperature dependences $\varepsilon(T)$; indeed, the relatively weak variation of $\varepsilon(T)$ upon a decreased temperature in it is replaced by a more pronounced decrease of the permittivity, and at $T \approx 120$–150 K the $\varepsilon(T)$ curves pass through a minimum. A break is observed in the $\varepsilon(T)$ curve for pure C_{60} at $T \approx T_I = 260$ K. Further decrease of temperature is accompanied by a growth of $\varepsilon(T)$ for all the samples studied, with a distinct maximum appearing at $T \approx T_{II} = 90$ K in the temperature dependence of the permittivity. Interestingly, a number of the samples exhibit for $T < T_{II}$ one more feature in $\varepsilon(T)$, i.e., a low-temperature segment of growth starting at $T \approx T_{III} = 25$ K, with the permittivity not saturating down to the liquid helium temperature (see figure).

The temperature behavior of $\varepsilon(T)$ of various molecular complexes is specific, first, in the absolute magnitude of ε [$(S_4N_4)_{1.2}C_{60}(C_6H_6)_{0.8}$ has the largest values of ε]. One also sees that, within the $200 < T < 260$ K interval, the shape of the $\varepsilon(T)$ curve and, in particular, the slope $\frac{\partial\varepsilon}{\partial T}$ depend apparently on donor type (see figure). However, the variations of $\varepsilon(T)$ within this temperature range are comparable to the absolute error of ε measurement in our experiments, which does not permit a final conclusion on the relation of the slope $\frac{\partial\varepsilon}{\partial T}$ to composition. Note that the low-temperature anomaly in $\varepsilon(T)$ at $T \approx T_{III}$ was observed by us to exist in all the materials studied, including pure C_{60}, with the exception of the $(BTX)C_{60}CS_2$ complex.

In the region of $T > 120$ K, the temperature dependences $\varepsilon(T)$ agree qualitatively with the data obtained earlier for pure C_{60} [3]. However, $\varepsilon(T) \approx$ const for $T <$ 120 K [3, 5], whereas in our case one observes a maximum in $\varepsilon(T)$. Besides, published data do not mention the low-temperature feature in the permittivity at $T_{III} \approx 25$ K.

4. The experimental data obtained in this work on the dielectric permittivity of C_{60}-based molecular complexes permit several conclusions.

Firstly, the $\varepsilon(T)$ curves exhibit distinct features at $T = T_{II}$ for all the samples studied, whereas the feature at $T = T_I$ is observed only in pure C_{60}, and is practically not seen in the molecular complexes at all. Thus, although the orientational disorder in C_{60}-based molecular complexes is believed to be frozen [6, 8, 9], the existence of clearly pronounced temperatures characteristic of a transition to the glassy state (T_{II}) in pure C_{60} suggests that some features of this transition persist in these compounds too. The C_{60}-based molecular complexes apparently retain a certain orientational degree of freedom, which freezes out with decreasing temperatures in the form of a phase transition at $T = T_{II}$.

Secondly, the experiments reported before did not reveal a feature in $\varepsilon(T)$ in the form of a maximum at the temperature of transition to the glassy state. This stresses the importance of a comprehensive investigation into the dispersion in permittivity in the $\omega\tau \geq 1$ frequency domain, which will be the subject of our future studies. Besides, the absence of an $\varepsilon(T)$ feature at $T = T_{II}$ for $\omega\tau \ll 1$ [2, 3, 5] indicates that simple one-parameter dispersion models of the type of the Debye relaxator are applicable to C_{60}-based materials only in the range of relatively high temperatures ($T > 120$ K), whereas in the region of transition to the glassy state, $T \approx T_{II}$, more complex resonance-type models may turn out to be more adequate. Note that a similar conclusion was reached in [5].

Thirdly, the fact of the temperature dependences $\varepsilon(T)$ for different C_{60}-based materials prepared in different reactions by different techniques with similar patterns makes the conjecture [1, 5] of the dominant effect of oxygen impurity on the dielectric relaxation of fullerenes hardly likely. We believe, following [3, 12], that the temperature relations $\varepsilon(T)$ obtained reflect intrinsic properties of C_{60}-based materials.

In conclusion, consider the low-temperature anomaly in $\varepsilon(T)$ at $T \approx T_{III}$. The magnetic properties of the $(ET)_2C_{60}$ molecular complex [where ET stands for bis(ethylenedithio)tetrathiafulvalene] were found [12] to exhibit a feature in this temperature region, which correlates with the break in the temperature dependence of the permittivity similar to that shown in the figure. While the nature of the observed low-temperature behavior of $\varepsilon(T)$ remains unclear, the absence of this feature in the $(BTX)C_{60}CS_2$ complex, which differs from the other studied materials in that its C_{60} molecules are separated from one another, suggests a possible effect of the interaction between C_{60} molecules on the onset of the low-temperature anomaly.

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