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Dielectric relaxation dynamics in C_{60} and C_{70}

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Abstract

The electrical response of polycrystalline fullerites has been studied after annealing them under various conditions. Dielectric measurements have been carried out in the frequency range 100 Hz $< \nu <$ 1 MHz and for temperatures 10 K $< T <$ 300 K. For C_{60}, electronic conduction, a phase transition and a dielectric relaxation process are clearly resolved. The latter is described by simple thermally activated behaviour but a broad spectrum of relaxation times, the origin of which is discussed. For C_{70}, no clear experimental evidence for a similar dielectric relaxation process could be found in the temperature and frequency regime investigated.

1. Introduction

Recently, the fullerenes, a new modification of carbon, have attracted considerable attention [1]. C_{60} (shaped like a soccer ball) and C_{70} (shaped like an American football) reveal an orientationally disordered crystalline phase at room temperature characterized by an almost free rotation of the quasi-spherical molecules. At $T_c \approx 255$ K (C_{60}) and $T_c \approx 280$ K (powdered C_{70}) they undergo structural phase transitions into orientationally ordered phases. However, even below the phase transition temperatures the molecules in both compounds undergo hindered reorientational motions. In C_{60}, the relaxation dynamics have been studied by a variety of experimental techniques, including nuclear magnetic resonance (NMR) [2], sound velocity [3], thermal expansion [4], heat capacity [5] and thermal conductivity experiments [6]. In the thermodynamic experiments [4–6], it has clearly been demonstrated that the freezing temperature strongly depends on the cooling rate as is typical for glass-forming materials. From these experiments, the energy barriers against molecular reorientation have been determined to be of the order of 260 meV and the similarities of the freezing process to the orientational glass transition [7] have been emphasized. Also in the NMR and the ultrasonic experiments, frequency dependent anomalies were detected [2,3]. Very unexpectedly, Alers et al. [8] were able to show experimentally that the molecular relaxation dynamics can be studied via dielectric spectroscopy. These authors suggested that dipolar moments may be induced by adjacent pairs of misoriented C_{60} molecules, as a consequence of the broken inversion symmetry of the orientationally ordered phase [8].

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In the present investigation, the reorientational motions of the C_{60} molecules in the solid state are studied in a broad frequency range also by means of dielectric spectroscopy. One purpose of the present work was to compare our dielectric results with the reorientation times as determined using the experimental techniques mentioned above. Another objective was to clarify whether the dipolar moment is an intrinsic property of the fullerite compounds or whether it is induced by impurity atoms, e.g., by oxygen which is easily absorbed by the fullerites, even at room temperature [9]. A further open question that is interesting to address concerns the degree of cooperativity of the freezing process. For the fullerites it is still unclear whether the rotational freezing has to be described as a single-molecule phenomenon which would imply that the hindering barriers are determined exclusively by the lattice anisotropy or whether multipolar exchange interactions play the dominant role. Experimental indications for the importance of cooperativity effects are often inferred from the observation of polydispersive relaxation behaviour or from deviations from a simple Arrhenius-type slowing of the relaxation times [10]. Finally it is of interest to find out whether dipolar relaxation effects can also be detected for C_{70}.

2. Experimental details

The real and the imaginary parts of the dielectric constant were recorded at audio frequencies (100 Hz $< \nu <$ 1 MHz) using autobalance bridges. Powdered samples, pressed into pellets (typical size 6 mm diameter × 0.2 mm) were used for our investigations. To remove residual solvents and other impurities, the pressed pellets were repeatedly heated in vacuum from room temperature to 600 K. The electrical conductivity, σ, was recorded during the thermal treatment which was terminated only after reproducible $\sigma(T)$ results were obtained. To study a possible sample dependence of the observed dipolar effects, some of the pellets were annealed in oxygen atmospheres of 2 bar pressure for several days. For the dielectric experiments, the samples were inserted between polished brass plates.

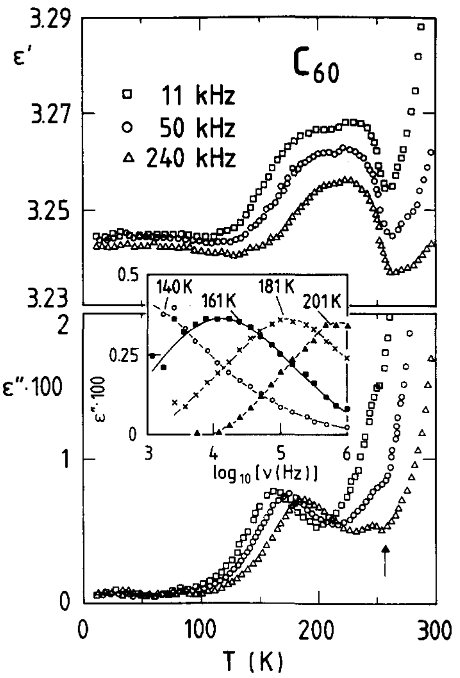

Fig. 1. Temperature dependence of the real and the imaginary parts of the dielectric constant in polycrystalline C_{60}. Upper frame: $\varepsilon'(T)$ at three frequencies as listed in the figure. Lower frame: $\varepsilon''(T)$ at three frequencies (same symbols as in upper frame). The arrow indicates the phase transition temperature. The inset shows the frequency dependence of $\varepsilon''(\omega)$ for several temperatures obtained by subtracting a linear (in T) conductivity background.

3. Results

Representative results of the temperature and frequency dependences of the real part ε' and the imaginary part ε'' of the dielectric constant are presented in Fig. 1. The upper frame of Fig. 1 shows the temperature dependence of ε' for three different frequencies. With decreasing temperatures, ε' increases steeply below 255 K which is clearly related to the order–disorder phase transition. The magnitude of the apparent increase in the dielectric constant of $\Delta\varepsilon'/\varepsilon' \approx 3 \times 10^{-3}$ is consistent with the contraction $\Delta l/l = (3\text{–}3.5) \times 10^{-3}$ of the lattice constants below T_c as deduced from diffraction [11] and dilatometry [4] experiments. At lower temperatures, 130 K $< T <$ 200 K, ε' exhibits a step-like decrease at temperatures that are lower the smaller the measuring frequency is. This behaviour is typical for an orientational slowing of dipolar degrees of freedom.

The signature of a dielectric relaxation process is seen even more clearly in the lower frame of Fig. 1 which shows the temperature dependence of ε'' for different measuring frequencies. At higher temperatures, the relaxation feature is superimposed on a strongly increasing conductivity background. The increase in the dielectric loss, $\varepsilon''(T) = \sigma(T)/\omega\varepsilon_0$, reveals the characteristic features of thermally activated hopping of electronic charge carriers across energy barriers which are determined predominantly by Coulomb interaction forces. The frequency independent anomalies at 255 K signal the structural order–disorder phase transition.

Results similar to those shown in Fig. 1 were obtained for a variety of samples from different sources and with different oxygen contents. The latter were mainly due to a variation of the annealing procedures and gas atmospheres. From the experiments we have performed so far, it is evident that the strength of the dipolar relaxation (which can be taken as a measure of the static dipolar susceptibility and hence of the number and magnitude of the dipole moments) depends on the sample history. However, it has to be clearly stated that the dipolar relaxation never was completely absent and that the relaxation times in all the samples investigated roughly follow the same T-dependence.

4. Discussion

For an analysis of the frequency dependence of the dielectric loss, we subtracted the conductivity background. The result is shown in the inset of Fig. 1. The dielectric loss peaks thus obtained exhibit half widths of $W = 2.2(\pm 0.2)$ decades. This finding clearly demonstrates the polydispersive character of the relaxation process and can be compared to the results of Alers et al. [8] on a single crystal of C_{60}. These authors analyzed $\varepsilon'(T)$ for $150\,\mathrm{K} < T_r < 180\,\mathrm{K}$ by assuming a Gaussian distribution of activation energies with a full width at half maximum (FWHM) of $\Sigma = 68$ meV. The width of the corresponding distribution of relaxation times is given by $\tilde{W} = \Sigma/(k_B T_r \ln 10)$ [12]. The width $\tilde{W} = 2.1(\pm 0.2)$ decades thus obtained from experiments on a single crystal [8] is consistent with the width from our study of C_{60} polycrystals.

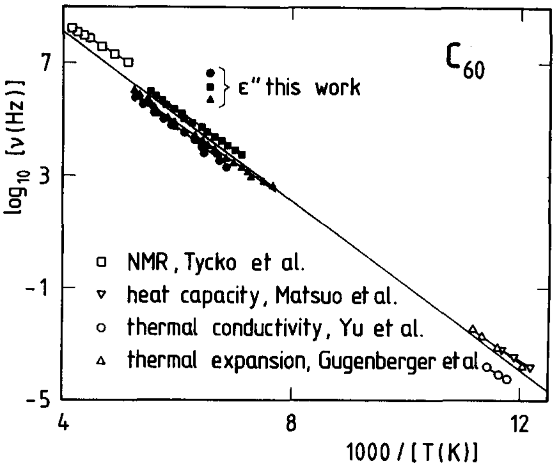

Fig. 2. Temperature dependence of the logarithm of the mean relaxation rate vs $1/T$ in C_{60}. Full symbols: dielectric results of the present investigation for three different samples; (□) NMR [2], (△) thermal expansion [4], (▽) heat capacity [5], and thermal conductivity results (○) [6]. The dielectric results of Alers et al. [8] are well within the range of relaxation rates as observed in our study.

The mean relaxation times of the reorientational motions were determined from the peak maxima in the conductivity-corrected $\varepsilon''(T)$. In Fig. 2 we plot the logarithm of the mean relaxation rate versus the inverse temperature for three different samples. The energy barriers against reorientations thus obtained vary from 275 meV to 311 meV; the attempt frequencies vary from 1 THz to 100 THz. Fig. 2 provides clear experimental evidence that the dielectric relaxation rates are consistent with the Arrhenius behaviour of the time constants as determined by different experimental techniques over 12 decades of measuring frequency [2,4–6]. Thus, all experiments, albeit operating at very different timescales, measure the same thermally activated process. The best guess of the underlying Arrhenius law which determines the common temperature dependence of the relaxation rates in C_{60} is given by $\nu = 75\,\mathrm{THz}\exp(-314\,\mathrm{meV}/k_B T)$. At the order–disorder phase transition temperature T_c, the mean relaxation rate is 170 MHz. Above T_c, the relaxation rate is strongly enhanced and the hindering barrier against molecular reorientations is significantly reduced [2,13].

In C_{70}, the $\varepsilon'(T)$ spectra (not shown) exhibit anomalies at the structural phase transition at 280 K. $\varepsilon''(T)$ is governed by conductivity contributions similar to those observed in C_{60}. However, as yet we have not obtained any results that provide clear evidence for a dipolar relaxation process for temperatures $10\,\mathrm{K} \leqslant T \leqslant 300\,\mathrm{K}$ and frequencies $100\,\mathrm{Hz} \leqslant \nu \leqslant 1\,\mathrm{MHz}$.

The mean relaxation rates in C_{60} follow a simple type of Arrhenius behaviour and we were able to demonstrate that the dielectric response is strongly polydispersive (cf. inset to Fig. 1). It is interesting to compare these observations with the findings in other orientationally disordered solids. In the family of supercooled plastic crystals of which C_{60} is a member, Arrhenius behaviour and single exponential relaxation are correlated [10]. Very recent low frequency mechanical measurements indeed reveal evidence for monodispersive elastic behaviour [14]. In order to understand the polydispersivity seen in the dielectric experiments, we note that, in systems governed by thermally activated dynamics, deviations from Debye behaviour are often due to the presence of static random fields [10]. In the fullerites, random electric fields may be due to, for example, interstitial oxygen impurities, which strongly affect the electrical properties but which apparently have no detectable effect on the elastic response.

5. Summary and conclusions

The main findings of our dielectric studies of C_{60} are the following

(i) Clear signatures of the phase transition show up in the real as well as in the imaginary part of the dielectric constant.

(ii) The dielectric relaxation in our polycrystalline samples is similar to that reported for single crystals [8].

(iii) The dielectric mean relaxation times are in accord with the results obtained by other techniques. The rates can be described by $\nu_{\mathrm{peak}} = 75\,\mathrm{THz}\cdot\exp(-314\,\mathrm{meV}/k_{\mathrm{B}}T)$ over a range of twelve decades in frequency.

(iv) The dielectric loss peaks are $W = 2.1(\pm 0.2)$ decades wide. Such a behaviour is unusual for supercooled plastic crystals in which the relaxation rates follow an Arrhenius law. This observation indicates the presence of random electric fields, possibly due to oxygen impurities.

(v) The magnitude of the peaks in ε'' but not their position depends on the annealing conditions.

Finally, in C_{70} the phase transition shows up as an anomaly in the real part of the dielectric constant. However, no well defined dipolar relaxations could be detected so far.

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