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Phase transitions of CO-intercalated C_{60} crystals

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Abstract. – We report the temperature dependence of the specific heat of $(CO)_xC_{60}$, and the temperature dependence of the lattice parameter, as determined by X-ray powder diffraction. A first-order phase transition and a glass transition are found to occur at temperatures below the corresponding transition temperatures of pure C_{60}. The transition temperatures depend on x. Specific-heat measurements on a sample with $x \approx 0.5$ show the orientational ordering transition at $T_c = 248.8$ K and the glass transition at $T_g = 83.9$ K. Contrary to pure C_{60}, the temperature dependence of the lattice parameter of $(CO)_xC_{60}$ ($x \approx 0.67$) does not show an anomaly at the glass transition, which is explained by the already expanded lattice of $(CO)_xC_{60}$. The energy difference between major and minor orientations is determined as 19.1 meV.

It is well established by now, that C_{60} crystals undergo a first-order, rotational ordering transition at $T'_c = 261$ K, and that they show a glass transition at $T'_g \approx 90$ K. It has been realized that the transition temperatures and the pre-transitional effects sensitively depend on the purity of the samples. The influence of impurities like solvent molecules, oxygen and nitrogen has been studied extensively [1-4]. Generally, it has been observed that in less pure samples, the first-order phase transition occurs at lower temperatures and that pre-transitional effects become more pronounced [3,4]. Furthermore, the transition has been found to be affected by stacking faults and by impurities replacing the C_{60} molecules, *e.g.*, C_{70} [5,6].

Recently, it was reported that microcrystalline C_{60} can be intercalated with CO gas in a reversible way to form the Van der Waals compound $(CO)_xC_{60}$ [7]. X-ray powder diffraction at low temperatures showed that the crystal structure is similar to that of pure C_{60}, with

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the CO molecules occupying the octahedral sites in the cubic close-packed lattice of C_{60} [8]. The dynamics of the CO molecules was studied by IR and NMR spectroscopy [7, 9]. Being dependent on temperature and pressure, CO molecules were found in states of nearly free rotation, hindered rotation, and frozen-in disorder [7-9].

Alternatively CO can be considered an impurity in the C_{60} lattice, allowing the study of the effects of a well-characterized impurity on the properties of solid C_{60}. The effects on the phase transitions are then of particular interest. Our previous experiments did reveal the first-order transition, although an accurate value for the transition temperature was not determined [7,8]. However, none of the experiments showed any anomaly related to the glass transition. On the other hand, the ratio of occupations of the major and minor orientations of C_{60} as determined by X-ray diffraction at $T = 25$ K quantitatively match these ratios as deduced from IR spectra in the range 0.6 K to 10 K, thus suggesting the ratio of major to minor to remain constant at these temperatures. This implies a glass transition in $(CO)_xC_{60}$ above 25 K.

The glass transition of C_{60} has been observed as anomalies in the temperature dependence of the specific heat and of the lattice parameter [10, 11]. Therefore, we decided to perform corresponding experiments on $(CO)_xC_{60}$. As is reported here, both the rotational-ordering transition and the glass transition give rise to well-defined anomalies in the temperature dependence of the specific heat. It is found that both transitions are shifted towards lower temperatures as compared to pure C_{60}. Furthermore, the temperature dependence of the lattice parameter is presented, as measured by accurate X-ray scattering experiments. Contrary to pure C_{60}, the glass transition does not lead to any anomaly in the lattice parameter. The reasons for this discrepancy are discussed.

$(CO)_xC_{60}$ was synthesized as described previously [7]. For a reaction time of 8 days, a composition of $x = 0.67$ was determined by X-ray diffraction [8]. The same reaction circumstances applied to the sample that was used for the present X-ray scattering experiments. For the sample used in the measurements of the specific heat the reaction was done at a slightly higher temperature, but with 5 days exposure only. After completing the present experiments, it was found that the value of x depends on the reaction time more than on the reaction temperature, thus we estimated a value of $x = 0.5$ for this sample. For the measurements of the specific heat 195.6 mg of $(CO)_{0.5}C_{60}$ sample was sealed in a Duran-glass container of 285.3 mg under He gas at a pressure of 1 bar. The glass container was then attached to the sample holder with a small amount of Apiezon-N grease. The specific heat (C_p) was determined between 25 K and 300 K, by measuring the rate of heat transfer while applying a constant rate of increase of the temperature [12]. Due to the small heat capacity of the sample relative to the heat capacity of the container, only a limited accuracy was obtained for the absolute value of C_p. Nonetheless, the relative accuracy is better than 0.005 at 100 K. A rate of change of the temperature was chosen equal to 3 mK s^{-1}, and only small differences were found with runs performed with rates of 1.5 mK s^{-1} and 0.5 mK s^{-1}. The data were corrected for the contributions of the sample holder, sample container and the grease.

Figure 1 gives the specific heat as a function of temperature. The first-order transition is clearly visible at $T_c = 248.8$ K (temperature of the maximum in C_p). A shoulder is present on the low-temperature side. The same experiment was performed on a sample of 157.8 mg C_{60} from the same batch, but not exposed to CO. For this compound the first-order transition is found at $T'_c = 259.4$ K, and a shoulder was not found. This shows that the concentration of impurities is low in our pristine C_{60}, and that the observed shift of T_c as well as the occurrence of the secondary maximum can be attributed to the presence of CO.

By integrating the peak in the interval from 215 K to 260 K for $(CO)_xC_{60}$, and from 225 K to 265 K for C_{60}, the enthalpy of transition (ΔH_{tr}) and the entropy of transition (ΔS_{tr}) were determined. For $(CO)_xC_{60}$ we obtained $\Delta H_{tr} = 6.2$ kJ mol^{-1} and $\Delta S_{tr} = 25.2$ J K^{-1} mol^{-1}

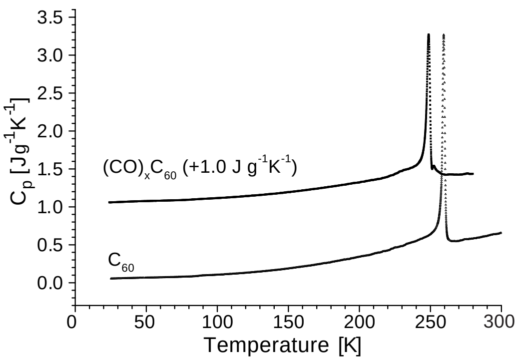

Fig. 1

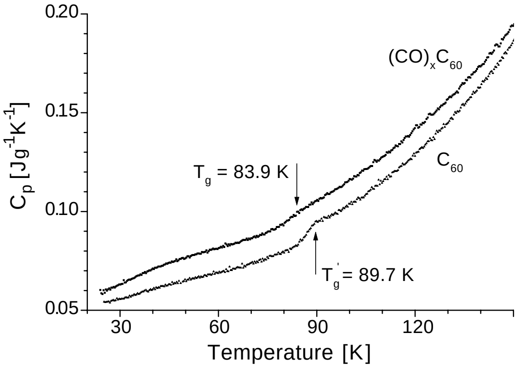

Fig. 2

Fig. 1. – Specific heat of $(\mathrm{CO})_x\mathrm{C}_{60}$ with $x \approx 0.5$ (upper curve) and of C_{60} (lower curve) as a function of temperature. For $(\mathrm{CO})_x\mathrm{C}_{60}$ the values of C_p are shifted by 1.0 J $\mathrm{g}^{-1}\mathrm{K}^{-1}$. The small anomaly at 250 K for $(\mathrm{CO})_x\mathrm{C}_{60}$ is due to experimental problems not related to the samples. It does not affect the derived entropy and enthalpy of transition.

Fig. 2. – Temperature dependence of the specific heat C_p in an interval around the glass transition for $(\mathrm{CO})_x\mathrm{C}_{60}$ with $x \approx 0.5$ (upper curve), and for C_{60} (lower curve).

($M = 734.665\ \mathrm{g\,mol}^{-1}$ for $x = 0.5$) and consequently for C_{60} $\Delta H_{\mathrm{tr}} = 6.3\ \mathrm{kJ\,mol}^{-1}$ and $\Delta S_{\mathrm{tr}} = 24.8\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$. Both values for ΔS_{tr} are close to $3R = 24.94\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$.

In accordance with previous studies, the measurement on the C_{60} sample shows that C_p below the transition did not return to the same base-line [3]. The same effect is also observed for the $(\mathrm{CO})_x\mathrm{C}_{60}$ sample. This can be understood in terms of a continuously changing order parameter, which in the present case is the difference between the occupations of the major and the minor orientations of the C_{60} molecules. A consequence is that the area under the peak in $C_p(T)$ cannot be determined unambiguously, as the contributions of the first-order transition and the variation of the order parameter below T_{c} cannot be separated. Accordingly, the value of ΔH_{r} of C_{60} compares favourably with the value of 7.0 (1) kJ mol^{-1} reported by De Bruijn *et al.* [13]. It is in even better agreement with 6.5 kJ mol^{-1} obtained by Pitsi *et al.* [3] for the integration over the interval 253 K to 273 K. It is larger than the value of 5.3 kJ mol^{-1} reported by Fischer *et al.* [4], who used an interval of integration of 5 K only. By extending the definition of the peak area towards the interval 180 K through 266 K, our value of ΔH_{tr} increases towards 7.3 kJ mol^{-1}. It follows that the differences obtained in the various experiments will be due to the different choices of the method of integration, rather than due to differences in the rate of variation of the temperature during the experiments. Because the heat and entropy of the transition should not include the contributions of the change in the order parameter below T_{c}, the true value for ΔH_{tr} will be closer to the smaller values reported, rather than to the larger values obtained with a wider interval of integration.

Figure 2 shows $C_p(T)$ at low temperatures. The glass-transition is found as a discontinuity of the derivative. For $(\mathrm{CO})_x\mathrm{C}_{60}$ it is found at $T_{\mathrm{g}} = 83.9$ K, which can be compared with a value of $T'_{\mathrm{g}} = 89.7$ K as presently observed for pure C_{60}. The latter value is in accordance with those reported previously [11]. It is found again that the presence of CO suppresses the transition towards a lower temperature.

Accurate X-ray powder diffraction measurements with synchrotron radiation have been performed to determine the thermal evolution of the lattice parameter of $(\mathrm{CO})_{0.67}\mathrm{C}_{60}$ (fig. 3).

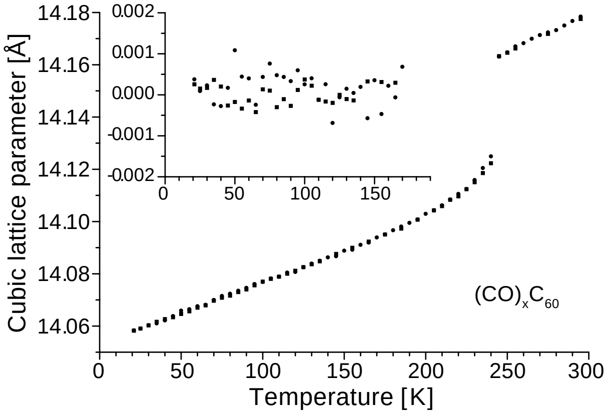

Fig. 3. – The cubic lattice parameter of $(CO)_xC_{60}$ for $x \approx 0.67$ as a function of the temperature. Squares are points obtained in the cooling run, and circles are points obtained in the heating run. The values were determined from the positions of the (422) Bragg reflection in the X-ray powder diffraction patterns. The zero-point correction and the correction for the asymmetry of the peak were applied according to the fit to the (101) Bragg peak of α-quartz, which was added to the sample as internal standard. The standard deviation is estimated as 0.0001 Å. The measurement was repeated in steps of 5 K. The inset shows the difference between the measured lattice parameter and the value of a straight line obtained by a least-squares fit to the data in the interval 20 K through 155 K.

(Experiment at beamline X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory.) The rotational ordering transition is found to occur between 240.0 K and 245.0 K, leading to an estimated transition temperature of T_c (X-ray) $= (242.5 \pm 2.5)$ K. This value is lower than the one found from the measurement of the specific heat, which we ascribe to the different amounts of CO present in the two samples. The jump of the lattice parameter at T_c is 0.040(1) Å, similar to the value reported for pure C_{60} [14].

The glass transition in C_{60} was discovered by the observation of an anomaly in the temperature dependence of the lattice parameter [10]. For $(CO)_xC_{60}$ the glass transition does not show up in the thermal evolution of the lattice parameter (fig. 3), although the specific-heat measurements clearly show such a transition, and we have observed the glass transition of C_{60} in the temperature dependence of the lattice parameter under similar experimental conditions [8].

We believe that the major effect responsible for this apparent discrepancy is that the lattice parameter of $(CO)_xC_{60}$ is larger than that of C_{60} (the difference is 0.013 Å at 25 K for $x = 0.67$) [8]. David *et al.* [14] have determined that the lattice parameter of a C_{60} crystal with all molecules in the major orientation is larger than the lattice parameter of a crystal with all molecules in the minor orientation, by an amount of 0.044 Å. As the observed lattice parameter of $(CO)_{0.67}C_{60}$ at 25 K is already substantially larger than that of an all major crystal of C_{60} at 25 K, it follows that the effect of different amounts of major and minor orientation on the lattice parameter will be smaller, or even unobservable. This is further supported by the observed nearly linear temperature dependence of the lattice parameter in the region between 20 K and 175 K (fig. 3).

An alternative explanation would be that the larger value for the occupation of the major orientation in $(CO)_xC_{60}$ compared to C_{60} could result in a smaller value for the derivative of this occupation with respect to the temperature. The effect of the glass transition on the thermal expansion then would be accordingly smaller. We have calculated these derivatives for both compounds at the temperatures of their glass transitions, using the values derived for the energy difference between the major and minor orientations (see below for $(\mathrm{CO})_x\mathrm{C}_{60}$ and ref. [14] for C_{60}). It turned out that they are of comparable size, with values of 0.0021 K^{-1} and 0.0026 K^{-1}, respectively. It follows that the difference in occupations of the major orientation in the two compounds cannot be the origin for the absence of the anomaly in the thermal expansion.

Further information on the thermal evolution of the structure follows from complete structure determinations. In addition to the structure at 25 K reported previously [8], we now have refined the crystal structure of $(\mathrm{CO})_x\mathrm{C}_{60}$ against diffraction data measured at 150 K. The same procedure was followed as for the analysis of the 25 K data [8]. The final refinement resulted in a fit with $R_\mathrm{p} = 0.037$ ($R_\mathrm{wp} = 0.062$ and $R_\mathrm{Bragg} = 0.071$). The C_{60} molecules were found distributed over the major and minor orientations again, but now with an occupation fraction of the major orientation of $P_\mathrm{major}(150\ \mathrm{K}) = 0.814(3)$. The lattice parameter refined to the value a (150 K) = 14.0815(2) Å. The occupation fraction of CO could not be refined, and it was fixed at the value determined at 25 K. Also the orientations of CO could not be determined accurately anymore, suggesting a considerable increase of the dynamics of this molecule as compared to low temperatures, in accordance with spectroscopic data [7].

The occupation fraction of the major orientation in $(\mathrm{CO})_{0.67}\mathrm{C}_{60}$ is larger than in pure C_{60}, both at 25 K and at 150 K. For C_{60} the occupation of the major orientation was found as 0.700 at 150 K [14]. Assuming a Boltzmann distribution, the energy difference between the two orientations can be derived as $\Delta G = 11.0$ meV, about equal to the value derived from a fit to the temperature dependence of P_major [14]. For $(\mathrm{CO})_x\mathrm{C}_{60}$ a similar analysis gave an energy difference between major and minor orientations of $\Delta G = 19.1$ meV. Using the occupation fraction determined at 25 K [8], and assuming this to be the equilibrium value at the glass temperature, lead to $\Delta G = 18.3$ meV.

Considering that the lattice of $(\mathrm{CO})_x\mathrm{C}_{60}$ is expanded as compared to the lattice of C_{60}, one would expect that ΔG decreases. The observation that an almost twice as large energy difference is found in $(\mathrm{CO})_x\mathrm{C}_{60}$ can only be explained by the stabilization of the major orientation of C_{60} by CO. This conclusion is supported by calculations of the lattice energy of C_{60}, employing the same method as used previously [7]. In the presence of one CO molecule the energy of a C_{60} molecule in the major orientation is lower than the energy of a molecule in the minor orientation by a value between 2 and 3 meV. For six octahedral sites around each C_{60}, and with $x = 0.67$, this leads to a calculated energy difference of around 10 meV, in fair agreement with the experimental difference of 8.1 meV at $T = 150$ K.

The reorientations between major and minor orientations furthermore depend on the activation energy for the reorientational jump ($\Delta G^{\#}$). Again, the expanded lattice would correspond to a smaller value of $\Delta G^{\#}$ in $(\mathrm{CO})_x\mathrm{C}_{60}$ as compared to C_{60}, and this is the rationale for the observed shift of the glass transition towards lower temperatures.

In conclusion, a study of the thermodynamics of a CO-intercalated sample of C_{60} revealed the influence on crystalline C_{60} of a well-defined impurity, which can enter and leave the octahedral cavities in a reversible way. We have shown that a major effect is a shift of both the first-order transition and the glass transition towards lower temperatures. The size of the shift depends on the composition x. Furthermore, the first-order transition in $(\mathrm{CO})_x\mathrm{C}_{60}$ is slightly broadened as compared to the transition in C_{60}. These observations are different from those in previous experiments on "dirty" C_{60}. There, strong pre-transitional effects in $C_p(T)$ below the first-order transition or even a complete smearing of this transition were ascribed to the effect of intercalated impurities. Our experiments show that the simple intercalation of a small molecule cannot be responsible for those dramatic effects, and it is likely that the smearing of the transition as observed previously is due to other processes, for instance partial oxidation of the C_{60} molecules. X-ray structure determinations have shown that the occupation of the major orientation of C_{60} is larger when CO is present. Evidence has been presented for a definite but small attractive interaction between CO molecules and C_{60} molecules in the major orientation, leading to a larger energy difference ($\Delta G = 19.1$ meV for $x = 0.67$) between the major and minor orientations in $(CO)_xC_{60}$ crystals.

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