

Compressibility of CO intercalated C_{60} crystals

Sander van Smaalen ^{a,*}, Robert E. Dinnebier ^a, Ronald Milletich ^b, Martin Kunz ^b,
Iwan Holleman ^c, Gert von Helden ^c, Gerard Meijer ^c

^a *Laboratory of Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany*

^b *Laboratory of Crystallography, ETH-Zentrum, CH-8092 Zürich, Switzerland*

^c *Department of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen, The Netherlands*

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Abstract

We report the pressure dependence of the cubic lattice parameter of $(CO)_x C_{60}$ at different temperatures, as determined by X-ray powder diffraction. In the measured range of pressures from 0.2 to 2 GPa, the volume is found to depend linearly on the pressure. The extrapolated volume bulk modulus of the ordered phase at room temperature is found to be $K_0 = -V dP/dV = 31.5(5)$ GPa. The bulk modulus at $T = 150$ K is found as $K_0 = 26.9(5)$ GPa. The greater stiffness at higher temperature is explained by the entropic contribution of the CO molecules to the bulk modulus. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Crystalline C_{60} fullerene is a relatively soft material with a bulk modulus of about $K_0(C_{60}) = 14$ GPa [1–4]. The dependence of the volume on pressure is non-linear. It has been fitted by equations of various types, all leading to similar values for the bulk modulus [3]. The pressure dependence of the transition temperature of the rotational ordering transition has been determined as $dT_c/dp = 164$ K GPa⁻¹ [5]. Thus, at room-temperature the ordering transition occurs at a pressure of about 0.2 GPa. Most studies did involve higher pressures, and the reported bulk moduli are values for the ordered phase. A recent study showed significantly lower values for $K_0(C_{60})$ for pressures smaller than about 0.1 GPa [4], and it

could be concluded that C_{60} is less stiff in its disordered phase than in the ordered phase.

Intercalated species greatly influence the properties of crystalline C_{60} under pressure [6]. Generally, intercalated molecules like oxygen and nitrogen, rare gas atoms and alkali atoms have been found to stiffen the C_{60} lattice, while leading to lower transition temperatures and a weaker dependence of T_c on pressure [3].

Recently, $(CO)_x C_{60}$ was synthesized, and its properties were studied by infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) [7]. X-ray powder diffraction showed that the CO molecules enter the C_{60} lattice at the octahedral sites [8]. The C_{60} lattice is slightly expanded, and both the ordering transition and the glass transition occur at lower temperatures, as compared to pure C_{60} [9]. At room temperature the CO molecules are dynamically disordered, but at $T = 25$ K CO molecules are frozen

* Corresponding author. E-mail: smash@uni-bayreuth.de

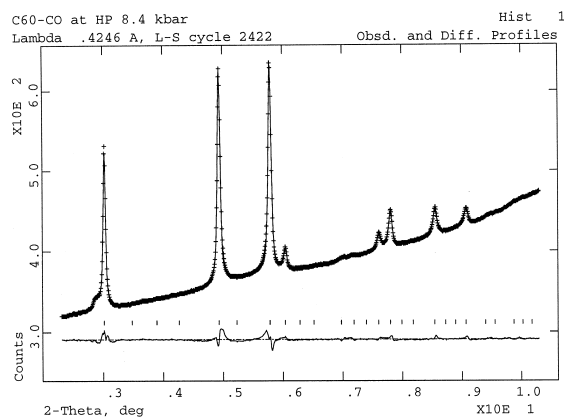


Fig. 1. X-ray powder diffraction scattering profile of $(\text{CO})_{0.67}\text{C}_{60}$ in a diamond-anvil cell at $p = 0.84$ GPa and $T = 295$ K. The scattering by the pressure cell has been subtracted. The solid line through the data points represents a LeBail-type of fit to the data. Reflection markers and the difference between data and fit are shown too. The major part of the differences between experimental and calculated profiles is ascribed to stacking faults. Improving the fit is not possible, because the latter property cannot be modelled by any of the available peak-profile functions.

into well defined positions, leading to a statistical distribution of CO molecules over six equivalent orientations [8,10]. Increasing pressure gradually suppresses the dynamics of the CO molecules at room temperature [11]. Here we report the pressure dependence of the lattice constant of $(\text{CO})_x\text{C}_{60}$ at $T = 295$ K and $T = 150$ K.

$(\text{CO})_x\text{C}_{60}$, with $x = 0.67$, was synthesized as described previously [7]. X-ray powder diffraction measurements were performed at beamline ID30 of the European Synchrotron Radiation Facility (ESRF), using radiation with a wavelength of $\lambda = 0.4246$ Å. For the experiments at room temperature, a diamond-anvil high-pressure cell (DAC) was loaded with the sample and with silicone oil as a pressure transmitting medium. Pressures were determined by monitoring the fluorescence of a small piece of ruby that was loaded together with the sample. The wavelength-shift calibration of Mao et al. [12] was used. The special design of the DAC allowed pressure settings above approximately 0.2 GPa only, thus precluding a study of the pressure dependence of the ordering transition. Due to freezing of the pressure medium, pure hydrostatic conditions existed only for pressures less than approximately 2 GPa.

X-ray scattering was recorded with imaging plates. The computer program FIT2D by Hammersley [13] was used to extract a profile of scattered intensity against 2θ , that was free of scattering effects of the different parts of the DAC. Nevertheless, the background was much higher than without the pressure cell, and only a few lines could be identified unambiguously. The scattering profile obtained at $p = 0.84$ GPa and $T = 300$ K is given in Fig. 1. This information is used to obtain an accurate value for the cubic lattice constant at each pressure. It appeared to be insufficient to refine the structure, e.g. to derive the orientations of the C_{60} molecules.

For the measurements at $T = 150$ K the DAC was placed in a liquid-helium cryostat. The cryostat led to a further increase in background scattering, thus reducing the accuracy of the extracted lattice constants (Fig. 2). Due to experimental problems data were collected only for pressures exceeding 0.5 GPa.

The results are summarized in Fig. 3. The large reduction of the volume at room temperature going from 0 GPa to about 0.2 GPa is attributed to the ordering transition. At ambient pressure this transition was found in $(\text{CO})_x\text{C}_{60}$ at a slightly lower temperature than it occurs in pure C_{60} [9]. Because the transition in pure C_{60} occurs at room temperature for a pressure of about 0.2 GPa, one might expect a similar value for $(\text{CO})_x\text{C}_{60}$ – as is measured indeed.

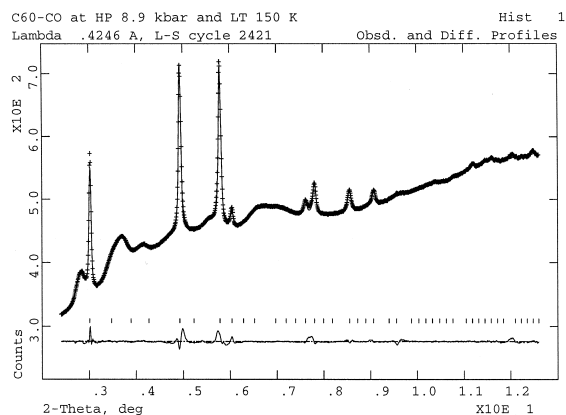


Fig. 2. X-ray powder diffraction scattering profile of $(\text{CO})_{0.67}\text{C}_{60}$ in a diamond-anvil cell at $p = 0.89$ GPa and $T = 150$ K. The scattering by the pressure cell has been subtracted. The extra structure as compared to Fig. 1 is due to scattering off the cryostat.

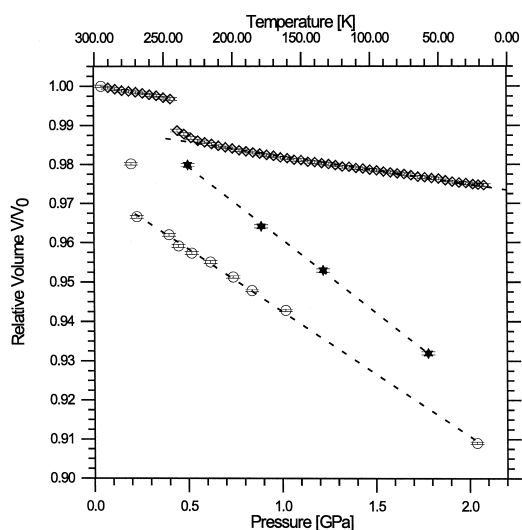


Fig. 3. Dependence of the volume of the unit cell of $(\text{CO})_{0.67}\text{C}_{60}$ on the temperature and on the pressure. Diamonds describe the temperature dependence (upper scale; after [9]). Circles and stars describe the pressure dependence (lower scale). Circles were obtained for $T = 295$ K. For $p > 0.3$ GPa the volume depends linearly on pressure, as described by $V/V_0 = 0.9743 - 0.0318p$. Stars were obtained for $T = 150$ K. A linear fit was obtained with $V/V_0 = 0.9981 - 0.0372p$ (the pressure p is to be given in GPa).

The scarce data in this region prohibit a precise determination of the transition pressure at room temperature or of dT_c/dp .

It is evident from the data that there is a linear appearance of the dependence of volume of the unit cell on pressure, despite theory requiring a nonlinear behaviour. The volume bulk modulus is defined as $K_0 = -Vd p/dV$ at constant temperature and in the limit $p \rightarrow 0$. From the fit of a straight line to the data at $T = 295$ K, an extrapolated bulk constant for the simple cubic phase can be derived as $K_0(295 \text{ K}) = 31.5(5)$ GPa. In a similar way $K_0(150 \text{ K}) = 26.9(5)$ GPa is obtained (Fig. 3). For the observed range of compression values, the volume–pressure relation, is usually described by the Birch–Murnaghan equation [14]. We have fitted the room-temperature data by this equation, using the program EOSFIT by Angel [15], and obtained $V_0 = 2788(2) \text{ \AA}^3$, $K_0 = 33.0(12)$ GPa, and $K' = -2.0(7)$. Within standard deviations the bulk modulus thus obtained is equal to the value obtained by the linear fit, and the nearly linear behavior is confirmed. The Birch–Murnaghan equation leads to a much higher value for the standard

deviation of K_0 than the linear fit does. This is explained by the fact that the former contains 3 fit parameters, while the linear fit uses 2 parameters only.

The stiffness of the C_{60} lattice is increased by a factor of about 2 on intercalation of CO. The value for the bulk constant of $(\text{CO})_{0.67}\text{C}_{60}$ lies within the same range as the values for the bulk constants reported for alkali intercalated compounds A_xC_{60} [3]. A bulk constant of 79.4 GPa was determined for Ba_3C_{60} [16]. For that compound, deviations from a linear dependence of the volume on pressure were observed for pressures above ≈ 3 GPa only. Thus the present results fit into the picture obtained for other intercalated compounds.

A remarkable feature is that the data indicate that the lattice at 150 K is less stiff than at 295 K. This can be explained by an entropic contribution to the bulk modulus. IR spectroscopy has determined that the dynamics of the CO molecules at room temperature decrease on increasing pressure [11]. Lattice energy calculations showed that the state of lowest energy of fitting CO into the C_{60} lattice is not much affected by pressure, but that the heights of the barriers for rotation are increased [11]. This implies that the contribution of CO to the lattice energy is only weakly dependent on pressure, while the entropy is considerably reduced on compression. A major part of the contribution of CO to the stiffness of $(\text{CO})_{0.67}\text{C}_{60}$ thus comes from this entropic term. The dynamics of CO at low temperatures is already reduced for zero pressure, and any entropic contribution to the stiffness will be smaller. This results in a smaller bulk modulus for 150 K than for 295 K, contrary to the behaviour of pure C_{60} [3].

In conclusion, we have determined the bulk modulus of $(\text{CO})_{0.67}\text{C}_{60}$. The value of K_0 at $T = 150$ K was found to be smaller than the value at $T = 295$ K. This could be explained as an entropic effect of the contribution of CO to the stiffness of the lattice.

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