Study of insulator to metal transition in Rb_4C_{60} by coherent and incoherent X-ray scattering under pressure

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Abstract

The equation of state (EOS) of Rb_4C_{60} is determined by high-pressure X-ray diffraction measurements. We observe an abrupt jump in the compressibility of Rb_4C_{60} between 0.5 and 0.8 GPa which is attributed to a structural phase transition preserving the tetragonal symmetry. Pressure effects on electronic density are studied by measuring Compton profiles below and above the transition. The ab initio calculation of the electronic structure is used to obtain theoretical equation of state, which agrees well with the experimental results. The calculations are used to quantitatively identify different contributions to the Compton profiles. In particular, we point out an unexpected contraction of the C_{60} molecular volume under pressure which brings about significant effects on the electronic density of Rb_4C_{60} compound.
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1. Introduction

The A_4C_{60} (A=K, Rb), which possesses bct structure [1], are perhaps the most interesting compounds among the A_xC_{60} family (x=1, 3, 4, 6) because they are non-magnetic narrow-gap insulators [2] that undergo a pressure-induced Mott insulator–metal transition at around 0.8 GPa [3]. Theoretical investigations invoke Coulomb repulsion, orbital degeneracy and Jahn–Teller effect [2] to explain their non-magnetic insulating character rather than the metallic nature expected from a band-structure picture [4].

In this article, we present a study of Rb_4C_{60} under pressure. The first goal is to study the crystal structure and obtain the equation of state for Rb_4C_{60}. While the EOS for Rb_3C_{60} has been measured by many groups, the EOS for Rb_4C_{60} remains unknown despite its great interest due to the

existence of a Mott transition in this compound at 0.8 GPa [3]. In this context, it is very important to know if a structural transition accompanies the Mott transition. The second goal is to follow the modification of the electronic density produced under pressure. Therefore, we performed Compton scattering experiments to measure the momentum density in Rb_4C_{60} at pressures below and above the insulator to metal transition (i.e. 0.2 and 2 GPa).

Fully relaxed, ab initio fully electronic structure calculation allows us to obtain a theoretical EOS, to compare with the measured results. Moreover, the wave functions obtained from calculations were used to calculate Compton profiles to be compared with our experiments. We have already demonstrated the utility of this approach in the case of intercalated fullerenes, in order to investigate behavior of the delocalized electron,, i.e. electrons responsible of bonding [5]. Specifically, the calculated Compton profiles are used in this paper to understand and quantify the different electronic contributions to the Compton profile, which include the unit cell contraction, the C_{60} molecule contraction and the molecular distortion under pressure.

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2. Compton scattering

Compton scattering involves the inelastic scattering of photons by electrons. The Compton profile, $J(q)$, is the projection of the electronic momentum density $n(p)$ onto the scattering vector. Within the impulse approximation, one assumes that the scattering is fast enough so that the interaction potential can be regarded as unchanged during the process. Within this approximation, the Compton profile is defined as

$$J(q, \mathbf{e}) = \int n(\mathbf{p})\delta(\mathbf{p}\cdot\mathbf{e} - q)d\mathbf{p} = \int \chi * (\mathbf{p})\chi(\mathbf{p})\delta(\mathbf{p}\cdot\mathbf{e} - q)d\mathbf{p} \tag{1}$$

where $\mathbf{e}$ is the unit vector along the scattering vector $\mathbf{K}$, $n(\mathbf{p})$ is the electron momentum density and $\chi(\mathbf{p})$, the electron wave function in momentum space,, i.e. Fourier transform of the wave function in real space [6–8]. Throughout this paper we shall use atomic units (a.u.), for which $\hbar = m = 1$.

3. Theoretical approach

We obtain the electronic structures and the theoretical equations of state of Rb_4C_{60} within density functional theory and the local density approximation (DFT–LDA), using PARATEC code [9,10]. We use norm-conserving pseudopotentials [11] with a plane wave basis with a 60 Ry cut-off. By increasing the cut-off to 80 Ry we found that the calculations were fully converged with forces changing less than 1.8×10^{-4} Ry/a.u. and stress less than 0.08 GPa.

The pseudopotentials for carbon included $2s^2 2p^2$ components and $4s^2 4p^6 4d^0$ configuration for rubidium. Within DFT–LDA materials are metallic with a small conduction band dispersion of approximately 0.5 eV. However, conduction electrons represent only 1/60 of total C_{60} valence electrons. The C_{60} molecules were fixed in the most symmetric configuration (standard orientation) [12], i.e. three double bonds are perpendicular to $\langle 100 \rangle$ directions and $\langle 111 \rangle$ directions pass through centers of hexagons. This choice induces an artificial orthorhombic relaxed structure with a small difference in a and b parameters (less than 0.04 Å).

For obtaining the theoretical Compton profile, the calculated ground-state wave functions are expanded in planewaves,

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}}(\mathbf{G})\exp[i(\mathbf{k} + \mathbf{G})\cdot\mathbf{r}] \tag{2}$$

where $\mathbf{G}$s are reciprocal lattice vectors. The directional Compton profile takes the following form:

$$J(q, \mathbf{e}) = \frac{1}{N}\sum_n \sum_{\mathbf{k}} \sum_{\mathbf{G}} |C_{n,\mathbf{k}}(\mathbf{G})|^2 \delta((\mathbf{k} + \mathbf{G})\cdot\mathbf{e} - \mathbf{q})\vartheta(E_n - E_f). \tag{3}$$

The summation $\mathbf{G}$ in this equation is over all the reciprocal lattice vectors for which the $C_{n,\mathbf{k}}(\mathbf{G})$s are non-negligible. The summation $\mathbf{k}$ is over the symmetry-reduced sector of the BZ of Rb_4C_{60} compound and is carried out using a tetrahedral interpolation method [13]. Due to the small size of the BZ for these compounds, a relatively coarse mesh of 13 points was sufficient for the BZ integration. The summation n is over the occupied states. The function ϑ cuts off this summation at the Fermi energy in the case of a metal or a semi-metal. Since the measurements are performed on powder samples, the comparison with experiment is made with an average theoretical profile obtained from four calculated directional profiles, i.e. (0 0 1), (0 1 0), (1 0 0), (1 1 a/c).

4. Experimental procedure

The diffraction experiment has been performed on powder sample of Rb_4C_{60} prepared at University of Nancy (France) [called Rb_4C_{60}-N] and the Compton measurements were carried out on a sample from University of Montpellier (France) [called Rb_4C_{60}-M].

Rb_4C_{60} powder was synthesized by first preparing the compound Rb_6C_{60} using a vapor-transport method [14]. Part of the Rb_6C_{60} was then used to prepare Rb_4C_{60} by direct reaction with additional stoichiometric amounts of pure C_{60}. All samples were checked at ambient pressure by X-ray diffraction. It is worthwhile recalling here that is not possible to prepare samples without traces of either fcc Rb_3C_{60} or bcc Rb_6C_{60} [3,15].

4.1. Crystal structure

The X-ray diffraction powder data were obtained at the ID-30 beam line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) by angle dispersive X-ray diffraction technique employing monochromatic ($\lambda = 0.3738$ Å) radiation and collected on an image plate detector (Mar345). All measurements were carried out at room temperature. In a glove box the sample was loaded in a membrane cell with a diamond culet of diameter 600 μm (Rb_4C_{60}-N) [16]. Pressure values below 5 GPa were measured by using the ruby fluorescence method with a precision of 0.05 GPa. The sample-to-detector distance and the image plate angles were analyzed using the ESRF Fit2D software [17], and images subsequently integrated in conventional intensity versus 2θ angle patterns.

Results of Le Bail fitting are presented in Fig. 1 at room pressure and temperature, with no pressure transmitting medium. The sample is a three phase assemblage, including Rb_4C_{60}, Rb_3C_{60} and $RbOH–H_2O$ (space group $Cmc2_1$). Some traces of Rb_6C_{60} were detected only for pressures above 1 GPa. Data were analyzed in two ways: (i) General Structure Analysis System (GSAS) in the Le Bail configuration [18] with unit-cell parameters, profile shape parameters and the individual Bragg intensities varied independently, and (ii) by fitting the position of four peaks of the Rb_4C_{60} bct structure, namely the (200), (301), (103), (222) reflections and, whenever possible, the (002), (211), (332), (402) and (622) reflections. The latter method is corroborated by the analysis of spectra below 0.56 GPa since they give results identical to those obtained by GSAS.

The pressure dependences of the lattice parameters (a and c) of Rb_4C_{60} are shown in Fig. 2. We notice that the