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Towards weighing individual atoms by high-angle scattering of electrons

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ABSTRACT

We consider theoretically the energy loss of electrons scattered to high angles when assuming that the primary beam can be limited to a single atom. We discuss the possibility of identifying the isotopes of light elements and of extracting information about phonons in this signal. The energy loss is related to the mass of the much heavier nucleus, and is spread out due to atomic vibrations. Importantly, while the width of the broadening is much larger than the energy separation of isotopes, only the shift in the peak positions must be detected if the beam is limited to a single atom. We conclude that the experimental case will be challenging but is not excluded by the physical principles as far as considered here. Moreover, the initial experiments demonstrate that the separation of gold and carbon based on a signal that is related to their mass, rather than their atomic number.

1. Introduction

The atomic-size probe of the electron beam in a scanning transmission electron microscope (STEM) can provide a wealth of information via the large variety of signals that can be recorded as a function of probe position [1,2]. Most of these signals are, in some way, connected to the atomic number of the atoms, or to energy levels within the sample. In this work, we consider electron-atom Compton scattering (EACS) [3], also called electron Rutherford (back-)scattering (ERBS) [4,5], as a new type of signal to be recorded in combination with a spatially resolved beam. We estimate the small change in energy of the beam electron when scattering to high angles in an elastic collision with the atomic nucleus, and we put a special focus on the angle ranges that should be accessible in today's instruments. Importantly, the energy change is directly connected to the mass, rather than atomic number, of the atom. Moreover, it is influenced by the motion of atomic nuclei. The Doppler broadening of the peaks would make it impossible to separate the peaks from nuclei of neighboring mass (possibly with the exception of the lightest elements [6]), if they are recorded simultaneously. However, if the primary beam can be limited to a single atom, the problem of separating partially overlapping peaks will be reduced to that of identifying the center position of a single peak with sufficient precision.

The recoil energy of electrons scattered to large angles was first measured by Boersch et al. [7] and it is influenced by Doppler broadening due to the atomic motion, even at zero Kelvin [8,4]. EACS was introduced by Vos et al. as an experimental technique to observe the motion of the nuclei in solids or molecules, and is an electron analog for neutron Compton scattering [3]. The process can be described by rather simple classical physics – elastic scattering of a fast electron with a moving target (the nucleus). Since an atomic nucleus is much heavier than an electron, the energy transferred in an elastic collision is small. Nevertheless, it can be detected for bulk samples and large scattering angles, and the energy loss is larger for lighter atoms [3,9–11]. As a similarly important aspect, the broadening and profile of the EACS provides direct information on the momentum distribution of the phonons [12,13], rather than on the associated energy levels, as probed e.g. by phonon electron energy loss spectroscopy (EELS) [14]. In fact, the energy transferred from a beam electron to an atom is responsible for the knock-on damage encountered in electron microscopes [15–23]. As some of us have shown recently, the knock-on damage process is indeed isotope dependent, and influenced by atomic motion [23].

Below, we consider the possibilities of EACS measurements in connection with a spatially resolved probe, and in scattering geometries that might be achieved in a STEM. We show calculations for carbon (^{12}C and ^{13}C), hydrogen as the lightest, and gold as a common heavy element. The detection of hydrogen by EACS has been demonstrated for large samples [24,11] and the possibility of a spatially resolved measurements was discussed recently [6]. If electrons scattered to arbitrary angles (e.g. 135°) can be brought

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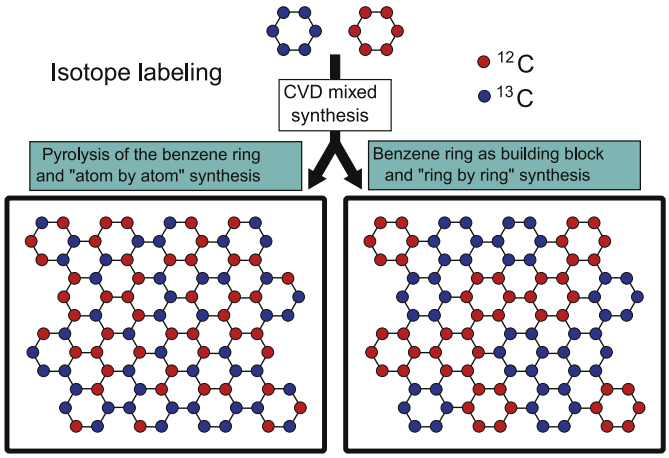

Fig. 1. Example motivation for isotope sensitive imaging of graphene, as a tool to understand synthesis mechanisms or chemical modifications.

into a spectrometer so that different elements are separated, EACS can be used a tool for compositional analysis [25]. Moreover, diamond and different orientations of graphite were distinguished by the broadening of the electron scattering peaks [13]. Combined with a spatially resolved probe, this opens not only an avenue to identify different phases of the same element, but also, at atomic-level resolution, possibly a new route to study vibrational states of atoms within defects. Ultimately, the capability to weigh atoms, and identify isotopes, would connect the powerful tools of isotope labeled chemistry with the atomic-resolution analysis in a scanning transmission electron microscope. In particular, we analyze here the precision and dose that would be needed to separate the two common isotopes of carbon, ^{12}C and ^{13}C. As an example for motivation, consider the growth of isotope-labeled graphene [26,27] from a molecular organic precursor (Fig. 1, for the example of benzene [28]): Conceivably, the carbon rings of the molecule might disassemble during synthesis and then reassemble into the graphene sample, or alternatively might stay connected as molecules (or fractions) which assemble into the 2-D honeycomb lattice. Synthesis from a mixture of isotopes [26,27], followed by atomic-resolution isotope-sensitive imaging, would shed unprecedented insight to the growth mechanism.

2. Basic principles

As motivated above, we consider scattering to large angles with the primary beam focused to smallest dimensions, as is possible in STEM experiments (Fig. 2a). Since the column geometry of existing instruments will allow electrons scattered up to ca. 10°, or 175 mrad to pass through the post-sample optics, special consideration is given to the "smaller" range of high-angle scattering. The primary beam of the STEM would ideally be focused to a single atom of the sample, which is possible with 2-D materials. Then, electrons scattered to low and high angles are simultaneously recorded in the spectrometer; i.e., the diffraction plane is condensed in one direction, energy-dispersed, and recorded on a 2-D detector. The obtained energy-momentum map would be recorded at every point of the scanned primary beam, thus creating a 4-D data set.

Since the incoming beam must be convergent, there will inevitably be an uncertainty in the measured scattering angle, i.e., spectra will be "washed out" in the angle- or momentum-direction. In addition, scattered electrons must be integrated over a certain range of angles, in order to obtain a finite signal. However, as we shown below, the main source of broadening is due to atomic vibrations. Hence, the separation of two peaks, such as those one from ^{12}C and ^{13}C, in the same spectrum would be impossible. However, if the primary beam can be located on a single atom, all that is needed is to determine the center position of a gaussian distribution to a sufficient accuracy. Here, it is crucial to realize that the center position of a peak can be determined with much higher accuracy than the resolution, only limited by the available signal to noise ratio.

We consider the electron scattering on the atomic nucleus in the coordinate system as shown in Fig. 2b. The atom is moving initially at a velocity $\mathbf{v} = (v_x, v_y, v_z)$ and we calculate the energy difference $E_{loss}(\theta) = E_e - E_{e'}$ between the incoming and deflected

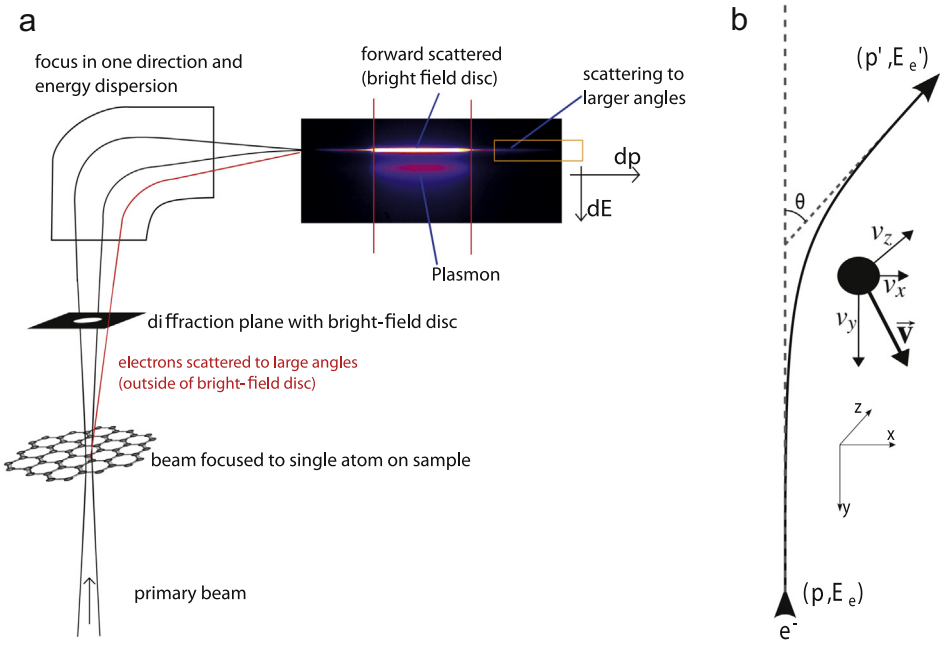

Fig. 2. (a) Schematic of the theoretically considered experiment (see the text). (b) Geometry and coordinate system as used in the calculations.