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Investigation on the reported superconductivity in intercalated black phosphorus

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ABSTRACT

Superconductivity intrinsic to the intercalated black phosphorus (BP) with a transition temperature T_c of 3.8 K, independent of the intercalant, whether an alkali or an alkaline earth element, has been reported recently by R. Zhang et al. (2017). However, the reported T_c and the field effect on the superconducting (SC) transition both bear great similarities to those for the pure Sn, which is commonly used for BP synthesis under the vapor transport method. We have therefore decided to determine whether a minute amount of Sn is present in the starting high purity BP crystals and whether it is the culprit for the small SC signal detected. Energy-dispersive X-ray spectroscopy results confirmed the existence of Sn in the starting high purity BP crystals purchased from the same company as in R. Zhang et al. (2017). We have reproduced the SC transition at 3.8 K in Li- and Na-intercalated BP crystals that contain minute amounts of Sn when prepared by the vapor transport method but not in BP crystals that are free of Sn when prepared by the high-pressure method. We have therefore concluded that the SC transition reported by R. Zhang et al. (2017) is associated with the Sn but not intrinsic to the intercalated BP crystals.

1. Introduction

Building on the work on graphene and a few other layered materials that followed, the two-dimensional layered black phosphorus (BP) has attracted great interest recently because of its scientific significance and device potential. Of particular interest is the tunability of its physical properties through varying the band structures by strain, electric field, number of layers, and intercalation. Superconductivity has also been predicted in electron-doped monolayer [1] and Li-intercalated bilayer phosphorene [2]. This culminated in the recent report by Zhang et al. [3] of superconductivity intrinsic to the intercalated BP with a transition temperature T_c of 3.8 K, independent of the intercalant, whether an alkali or an alkaline earth element. Indeed, this is an observation of a highly unusual superconducting state that is independent of the valence, the content, and the size of the dopant, in contrast to previous understanding of known superconductors. The authors attribute this so-called universal superconductivity to the heavily doped phosphorene layers with the intercalated layers serving as charge reservoirs, similar to the modulation doping in layered high temperature superconductors. The significance of the report is self-evident, if proven.

We have therefore examined the reported results [3] carefully and systematically. The intercalant-independent T_c of BP and the apparent small superconducting volume fraction of all samples investigated led us to the obvious question, *i.e.*, could the observed superconductivity be caused by a small superconducting contamination in the samples? Given the reputation of the group, contamination introduced during sample preparation seems to be highly unlikely. However, it is rather intriguing to find that the

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reported T_c of 3.8 K and the field effect on the superconducting transition both appear to be similar to those for the pure Sn [4]. The magnetic anisotropy reported is also too small to be consistent with the model proposed. It is also known that most of the commercially available BP crystals are prepared by transforming the red phosphorus through the chemical vapor transport technique with transport agents consisting of Sn or Sn-related compounds [5–8]. We have therefore decided to determine whether a minute amount of Sn is present in the starting BP crystals and, if yes, whether it is the culprit for the small superconducting signal detected.

2. Experimental

To determine if Sn-contamination can be introduced from chemical vapor transport synthesis, we have therefore started with three different BP crystal sources (BP-1, BP-2, and BP-3): BP-1 was purchased from Smart Elements in Germany, from which Zhang et al. obtained their BP crystals of the same purity (99.998%); BP-2 was prepared in our lab by the standard vapor transport method at ambient pressure; and BP-3 was made in our lab by the well-known high pressure technique [9].

2.1. Material synthesis

BP-2 crystals were prepared by converting the red phosphorus to black phosphorus by sealing appropriate amounts of red phosphorus (99.999%, Aldrich, 350 mg), Sn (99.99+%, Alfa Aesar, 35 mg), and I_2 (99.8+%, Fisher Scientific, 30 mg) in an evacuated quartz tube (12.7 mm in diameter, 127 mm in length), which was then placed in a tubular furnace with a temperature of 620 °C at the center and 27 °C at the end. Crystals of sizes up to ~3 mm × 1 mm × 0.5 mm were harvested at the cold end of the quartz tube.

BP-3 crystals were achieved by transforming red phosphorus powder (99.99+%, Aldrich, 0.28 g) wrapped in Au-foil under 1.5 GPa at 750 °C for 30 min followed by quenching to room temperature.

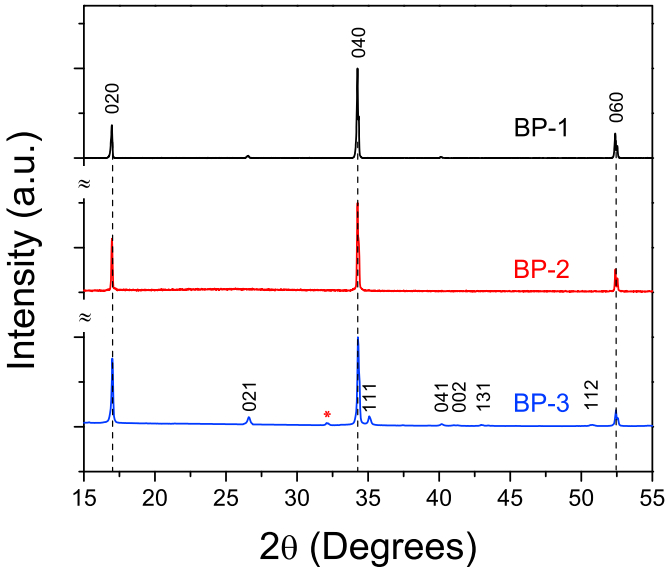

Fig. 1. X-ray diffraction spectra of starting BP-1, -2, and -3. * indicates the known peak for Au_2P_3.

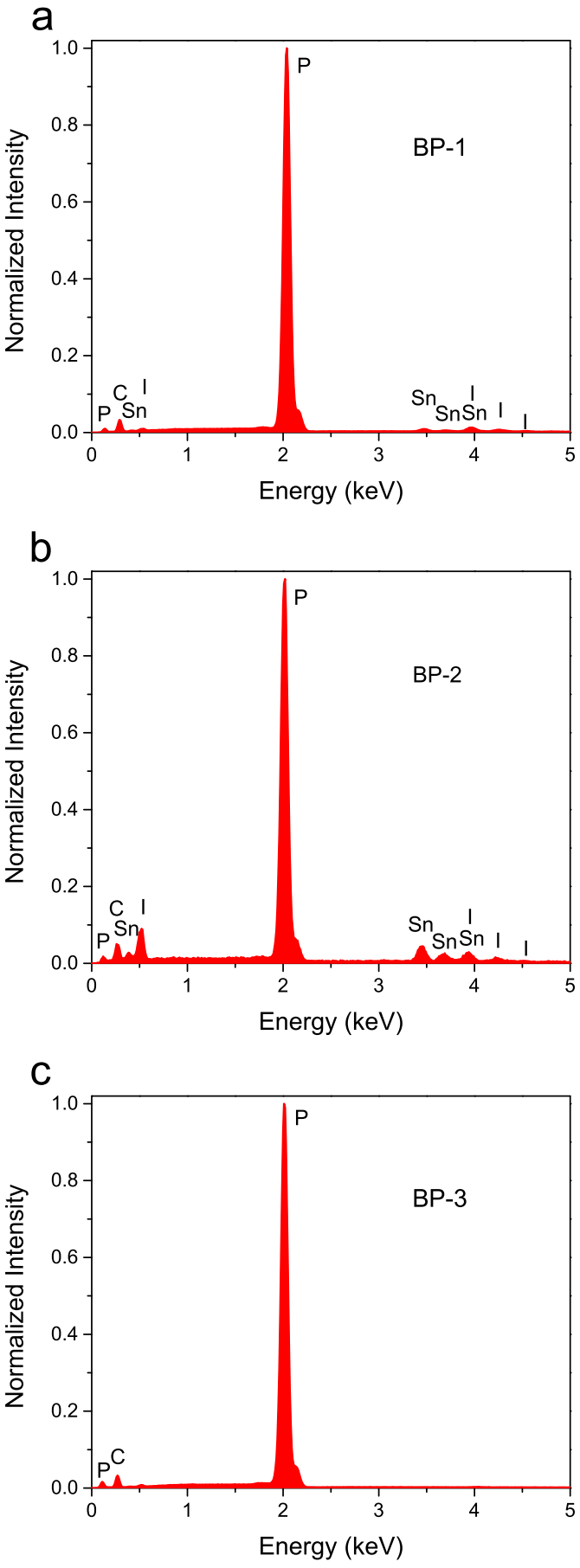

Fig. 2. EDS analysis for starting BP crystals. (a) BP-1. (b) BP-2. (c) BP-3.